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# A PROGRAM TO DEVELOP A HIGH-ENERGY DENSITY PRIMARY BATTERY WITH A MINI- MUM OF 200 WATT HOURS PER POUND OF TOTAL BATTERY WEIGHT

by

William E. Elliott, James R. Huff, Gerald L. Simmons,  
Guy D. McDonald, Judith L. Jamrozy and Warren L. Towle

prepared for

**NATIONAL AERONAUTICS AND SPACE ADMINISTRATION**

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SIXTH QUARTERLY REPORT  
October 1 - December 31, 1965

A RESEARCH REPORT FROM  
**GLOBE-UNION INC.**



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## SUMMARY

Lithium anodes were studied in  $\text{LiPF}_6$ -dimethylformamide and -N-nitrosodimethylamine electrolytes. In two dimethylformamide systems and one N-nitrosodimethylamine system, the solute had been dried prior to use. In the dimethylformamide systems, lithium exhibited greater polarization with the dried  $\text{LiPF}_6$  solute. Drying the solute did not significantly affect lithium performance in the N-nitrosodimethylamine electrolyte.

The investigation of cathode fabrication methods was continued with emphasis on decreasing the internal resistance losses in cupric fluoride cathodes. Four approaches to this problem were:

1. Sintering cupric fluoride on lightweight metal substrates.
2. Forming thin films of cupric fluoride on copper foil by solvent evaporation.
3. Electrodepositing thin cupric fluoride films on copper foil from hydrogen fluoride solutions.
4. Pressing small amounts of cupric fluoride (plus conductive additives and binders) on metal substrates at high pressures.

As a result of the sintering experiments, very thin electrodes with good mechanical integrity were produced. However, during electrochemical testing, these electrodes operated at more negative voltages than the cupric fluoride filter pad cathodes described in previous reports. These lower voltages may be a result of the absence of carbon which was incorporated in the filter pad cathodes.

The thin cupric fluoride film produced on copper foil by evaporating a methanol solution of cupric fluoride was evaluated by the linearly varying potential technique. Only a small amount of the active material was present and the scans were not definitive.

Electrodeposited cupric fluoride films were also studied by the linearly varying potential method. The curves indicated a strong possibility that reduction of copper oxide rather than copper fluoride was occurring.

Thin cathodes prepared by pressing small amounts of cupric fluoride plus conductive additives and binders at high pressures did not exhibit significantly improved electrochemical performance. This might possibly be due to the formation of impenetrable electrode surfaces as a result of the high formation pressures.

The effect of using different additives in cupric fluoride electrodes was also studied. Graphite, acetylene black, copper, silver, and antimony trifluoride were employed. The best results were obtained with small amounts (ca. 11 weight per cent) of acetylene black and antimony trifluoride.

Other inorganic cathodes investigated this quarter were a copper sulfide thin film electrode and a variety of pressed cathodes prepared from cobalt trifluoride, nickel difluoride, antimony trifluoride, titanium trifluoride, nickel hydroxide, iron oxide, nickel oxide, silver oxide, vanadium pentoxide, and copper sulfide.

These cathodes were evaluated in half-cell screening tests, coulombic efficiency tests, and linearly varying potential scans.

Electrochemical half-cell screening tests were conducted with dissolved active organic compounds. m-dinitrobenzene, trichloroisocyanuric acid (ACL-85), trichloromelamine, and hexachloromelamine were tested at different concentrations in a variety of electrolytes. The most promising of these compounds was hexachloromelamine which could sustain an 80ma/cm<sup>2</sup> discharge at a concentration of 1 molal in LiPF<sub>6</sub>-dimethylformamide (1 molal) at voltages more positive than -0.6V.

Linearly varying potential studies also indicated that these compounds are capable of sustaining high current densities. Coulombic efficiency tests were conducted for m-dinitrobenzene and trichloroisocyanuric acid. The latter compound yielded an efficiency of 70% at a concentration of 0.01 molal in LiPF<sub>6</sub>-N-nitrosodimethylamine (1 molal). The average discharge current was 1.9ma (or approximately 1ma/cm<sup>2</sup>).



As part of this overall program for characterization of vacuum-distilled solvents, refractive indices and specific conductivities were measured for vacuum-distilled N-nitrosodimethylamine fractions twelve weeks after distillation. Only slight changes occurred over the twelve week period.

Tri-n-propylamine was tested for its effectiveness in reducing the corrosion of lithium in dimethylformamide solutions. It was found that the rate of lithium consumption was decreased by addition of the amine to dimethylformamide.

Stability tests were completed for lithium and calcium in morpholinium hexafluorophosphate-dimethylformamide and -N-nitrosodimethylamine electrolytes pretreated with the anode metal. Lithium in pretreated morpholinium hexafluorophosphate-N-nitrosodimethylamine was the only stable system.

Linearly varying potential studies were made of  $\text{LiClO}_4$ -propylene carbonate,  $\text{LiCl}$ -dimethylformamide, and N-phenyl-N,N,N-trimethylammonium hexafluorophosphate-dimethylformamide. The scans of the dimethylformamide electrolytes showed reductions occurring in the -1.5 to -2.0V range. This would substantiate the hypothesis that electrolyte decomposition contributes to the coulombic output in certain full cell discharges.

Investigation of battery components was continued this quarter. Anion exchange membranes, filter paper, and an epoxy membrane were screened as separator materials. Polypropylene and polyethylene were tested for their stability in various electrolytes for possible use as case materials.

## INTRODUCTION

The objective of this research is to develop a primary battery with an energy density of at least 200 watt-hours per pound of total battery weight.

Preliminary electrochemical evaluations of calcium, lithium and magnesium anodes in various electrolytes have been virtually completed. Several promising combinations have been selected for a more thorough investigation.

Efforts have been made to improve the electrochemical characteristics of cupric fluoride cathodes. Concurrently, consideration has been given to possible approaches for eliminating some of the difficulties associated with conventional techniques of cathode fabrication. In addition, other cathode materials with high theoretical energy densities have been investigated.

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ABSTRACT

Lithium anodes were studied in  $\text{LiPF}_6$ -dimethylformamide and -N-nitrosodimethylamine electrolytes with "as received" and dried solute to determine the effect of drying the solute on electrochemical performance.

Various methods of sintering cupric fluoride on lightweight metal substrates were tried. Thin film cupric fluoride electrodes were prepared by electro-deposition and solvent evaporation. A copper sulfide thin film electrode was also made. Pressed inorganic cathodes containing conductive additives and binders were fabricated from the fluoride salts of antimony, cobalt, copper, nickel and titanium; iron, nickel and silver oxides; vanadium pentoxide; nickel hydroxide and copper sulfide.

Dissolved organic cathodes including N-chlorosuccinimide, 2,4-dinitrophenol, m-dinitrobenzene, trichloroisocyanuric acid (ACL-85), trichloromelamine and hexachloromelamine were studied.

Both inorganic and organic cathodes were evaluated in half-cell screening tests, coulombic efficiency tests, and linearly varying potential scans.

The characterization of vacuum-distilled solvents by measurement of changes in specific conductivity and refractive index was continued. Tri-n-propylamine was investigated as an anode corrosion inhibitor in dimethylformamide. Stability tests were carried out for lithium and calcium in electrolytes pretreated with the anode metal. Linearly varying potential studies were made of electrolyte decomposition.

Anion exchange membranes, filter paper, and an epoxy membrane were screened as separator materials. Stability tests were carried out for polypropylene and polyethylene case materials in various electrolytes.

I. OVERALL PROGRESS

## I. OVERALL PROGRESS

Progress during the Sixth Quarter encompassed work in the following areas:

### A. Anodes.

1. Effect of Drying the Solute on Electrochemical Performance of Lithium Anodes.

### B. Cathodes.

1. Fabrication and Electrochemical Half-Cell Screening.
  - a. Sintered cupric fluoride cathodes.
  - b. Thin film cathodes.
  - c. Pressed inorganic cathodes.
  - d. Dissolved active organic cathodes.
2. Coulombic Efficiency Studies.
  - a. Inorganic cathodes.
  - b. Dissolved active organic cathodes.
3. Linearly Varying Potential Studies.
  - a. Inorganic cathodes.
  - b. Dissolved active organic cathodes.

### C. Electrolytes.

1. Distillation and Characterization of Solvents Employed in Electrolytic Solutions.
2. Treatment with Inhibitors.
3. Stability of Anode Materials in Electrolytic Solutions.
4. Linearly Varying Potential Studies of Electrolyte Decomposition.

### D. Components.

1. Separators.
  - a. Anion exchange membranes.
  - b. Filter paper.
  - c. Epoxy membrane.
2. Case Materials.

A. Anodes.

1. Effect of Drying the Solute on Electrochemical Performance of Lithium Anodes.

During the sixth quarter, lithium anodes were studied in  $\text{LiPF}_6$ -dimethylformamide (DMF) and -N-nitrosodimethylamine (NDA) electrolytes according to the procedure described in the Third Quarterly Report. In three of the half-cell tests, the  $\text{LiPF}_6$  solute was dried prior to use. The purpose of the tests was not only to evaluate the capabilities of lithium anodes in  $\text{LiPF}_6$ -DMF and -NDA electrolytes, but also to determine the effect of drying the solute.  $\text{LiPF}_6$  was dried in two ways: first, by heating the salt at  $110^\circ\text{C}$  for 12 hours in a vacuum oven purged with nitrogen and, second, by heating the salt at  $110^\circ\text{C}$  for 24 hours in a nitrogen-purged, glass, drying apparatus. This apparatus consisted of a glass tube fitted near the bottom of the tube with a fritted glass disc. Nitrogen entered the tube through an opening below the disc and passed through the sample which was loosely packed above the fritted glass disc. An outlet, packed with glass wool, was located near the top of the tube.

As can be seen from the data in Table I, page IV-1, the electrochemical performance of lithium with undried  $\text{LiPF}_6$  in DMF was superior to that in the dried  $\text{LiPF}_6$  electrolyte. The lithium anode tested in undried  $\text{LiPF}_6$  in DMF could sustain at least a  $100 \text{ ma/cm}^2$  discharge at less than 50% polarization from the initial open circuit voltage. When dried  $\text{LiPF}_6$  was utilized, the maximum current densities which could be sustained at comparable polarizations were 1 and  $20 \text{ ma/cm}^2$ , respectively, for  $\text{LiPF}_6$  dried in a vacuum oven and  $\text{LiPF}_6$  dried in the apparatus described above. The changes in specific conductivity (see Table I for values of L) between the undried and dried systems do not seem large enough to cause this marked change in behavior.

The difference in electrochemical performance for lithium anodes in dried and undried  $\text{LiPF}_6$  in NDA was slight. Both systems could sustain discharges of at least  $100 \text{ ma/cm}^2$ . However, the lithium did not gas

upon insertion or during discharge in the dried  $\text{LiPF}_6$  system.

The data for the electrochemical half-cell testing of anodes is presented in Table I, pages IV-1 and IV-2. The  $\text{LiPF}_6(\text{undried})\text{-NDA}$  system was reported previously in the Fifth Quarterly Report and is included for comparison.

## B. Cathodes.

### 1. Fabrication and Electrochemical Half-Cell Screening.

#### a. Sintered Cupric Fluoride Cathodes.

Fabrication and electrochemical testing of cupric fluoride cathodes in past months has indicated the need for improved electrode conductivity and a decrease in internal resistance losses. Previous efforts were concentrated on enhancing electrode conductivity by the use of conductive additives. Methods of increasing electrode porosity were also investigated in an attempt to increase per cent utilization of the active material. This quarter, efforts were centered on decreasing internal resistance losses by producing "thin" cupric fluoride electrodes. Four methods were used: sintering  $\text{CuF}_2$  on lightweight metal substrates; forming  $\text{CuF}_2$  thin films by solvent evaporation; electrodepositing thin  $\text{CuF}_2$  films from HF solutions; and pressing small amounts of  $\text{CuF}_2$  plus conductive additives and binders on metal substrates. The latter two methods are described in sections B.1.b. and B.1.c.

Initial sintering experiments involved heating Cu and Al foil coated with thin layers of  $\text{CuF}_2$  in a nitrogen atmosphere. Temperatures ranged from 120 to 300°C. No sintering occurred even when the foil was roughened with emery paper to improve adhesion of the  $\text{CuF}_2$ .

It was decided that the application of pressure to the samples would be necessary to achieve sintering, i.e., "hot pressing."



A number of cathodes were prepared by spreading a thin layer of  $\text{CuF}_2$  which had been sifted through a 120 mesh sieve on a substrate and clamping the sample in a die. The die was then heated in a tube furnace for approximately two hours at  $200^\circ\text{C}$ . The furnace was purged with nitrogen to prevent any oxidation or formation of  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ .  $\text{CuF}_2$  was sintered on Cu and Al foil, Cu and Ni screen, and Al, Ag, and Ni expanded metal using this method. Cracking and separation of the  $\text{CuF}_2$  layer occurred in handling the Al foil sample because of its flexibility.

The Ni screen sample also exhibited poor adherence. The main difference between this and the other samples was that the Ni screen was not distorted by the application of pressure as was the case with Cu screen and Al, Ag, and Ni expanded metal. Thus, the Ni screen probably absorbed most of the pressure required to allow the  $\text{CuF}_2$  to fill in the void areas in the screen and sinter. The mechanical integrity of the other five samples was excellent.

Electrochemical half-cell screening tests were carried out for  $\text{CuF}_2$  sintered on Cu screen and Al, Ag, and Ni expanded metal. The details are given in Table II, page IV-3. Open circuit voltages were more negative than 0V vs.  $\text{Ag}/\text{AgCl}$  for all of the cathodes tested and polarization to voltages more negative than -1V occurred at current densities of less than  $1 \text{ ma}/\text{cm}^2$ .

In order to achieve better control of temperature and pressure, a second mode of sintering was tried. This method involved the use of a metallurgical press and a heated die. A temperature controller was used to set and maintain the maximum die temperature. Temperature readings were taken with a thermocouple. Pressure was measured with the gauge attached to the metallurgical press. This particular series of cathodes was not prepared in an inert atmosphere. However, the fit of the die parts was

such that only minimal amounts of moisture and oxygen should have diffused in to the hot  $\text{CuF}_2$  sample and the diffusion should have been slow. These assumptions were confirmed by the X-ray data wherein the patterns for copper oxides or  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  were weak or missing, depending on the length of time the sample was heated.

Sintered  $\text{CuF}_2$  electrodes were prepared on Ag expanded metal using the metallurgical press. The preparation consisted of placing the substrate (0.75" diameter) on the bottom face of the die and spreading a thin layer of sifted  $\text{CuF}_2$  over it. The die sleeve was fitted over the bottom of the die and the ram was inserted. The die was then inserted in the press and pressure and heat were applied to the sample. After the sintering operation was complete, the sample was allowed to cool while still under pressure to prevent exposure of the hot  $\text{CuF}_2$  to the atmosphere.

The experimental details and qualitative results for the hot press fabrication of  $\text{CuF}_2$  sintered cathodes in a metallurgical press are presented in Table III, pages IV-4 and IV-5. The data indicate that at a pressure of 8,900 psi, sintering can be effected with a decreasing amount of  $\text{CuF}_2$  decomposition as the sintering time is reduced. In tests 6 and 7, page IV-5, the samples were heated until the sintering temperature ( $150^\circ\text{C}$ ) was reached. A pressure of 8,900 psi was maintained. The samples were then rapidly cooled while still under pressure by means of a conduction cooling jacket. X-ray analyses indicated that both samples were pure  $\text{CuF}_2$ .

A problem which occurred with the metallurgical press method was that of release of the sample from the die. Spraying the die faces with Teflon did not improve the situation. "Sandwiching" the sample between pieces of filter paper did not ease

removal of the sample from the die but did produce an interesting side effect. At  $150^{\circ}\text{C}$  and 8,900 psi, the  $\text{CuF}_2$  became laminated to the filter paper. The resulting cathode, including the ingrained filter paper, retained its mechanical integrity over a 15 hour period in a  $\text{LiPF}_6$ -dimethylformamide electrolyte. The open circuit potential of +0.16V remained constant during this period. Because Teflon spray and filter paper failed to help release the sample, a Teflon tape was used to cover the die faces. The tape proved most satisfactory in reducing adherence of the sample to the die.

In general, attempts to fabricate sintered  $\text{CuF}_2$  cathodes were successful. Thin electrodes with good mechanical integrity were produced.

Coulombic efficiency studies were made of the various types of sintered  $\text{CuF}_2$  cathodes and are discussed in section B.2.a. Linearly varying potential studies are described in section B.3.a.

b. Thin Film Cathodes.

Copper fluoride and copper sulfide thin films on Cu foil were prepared this quarter. Copper fluoride thin films were formed by solvent evaporation and electrodeposition. The first technique consisted of placing a strip of Cu foil in a methanol solution of  $\text{CuF}_2$ . The solvent was evaporated, leaving a thin film of  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  deposited on the foil.

A solution of one gram of  $\text{CuF}_2$  in 250 ml of methanol was heated to reflux and filtered while still hot. A Cu strip was placed in a beaker containing the filtrate. The methanol was allowed to evaporate. A blue, relatively-adherent film of  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  remained on the Cu strip after evaporation. A portion of the Cu strip was heated for two hours at  $200^{\circ}\text{C}$  in a nitrogen atmosphere. The film turned green and some of the material separated from the

Cu substrate. A linearly varying potential scan was made of this cathode and is described in section B.3.a. Attempts were also made to produce thin  $\text{CuF}_2$  films in the same manner on Al and Ni substrates. The material deposited on the Al foil showed visible signs of decomposition. Deposits made on Ni were not adherent.

Electrodeposition was the second technique used to produce thin film  $\text{CuF}_2$  electrodes. Two strips of Cu foil were electrolyzed in a 48% HF solution. During the electrolysis, a red deposit was formed on the cathode and considerable gassing occurred. The deposit was identified by X-ray diffraction as  $\text{Cu}_2\text{O}$ . A black film, presumably  $\text{CuO}$ , was deposited on the anode initially. At this time, 1.1 amps were flowing at approximately 1.5V. This black film was gradually replaced by a white to colorless film which was identified by X-ray as  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ . A rapid change in current flow and voltage to 0.8 amps and 4.0 volts occurred as soon as the white film began to form. In the course of the electrolysis, the 48% HF electrolyte changed from a clear, colorless solution to a blue solution. Linearly varying potential studies were made of the three types of deposits and are described in section B.3.a.

A copper sulfide thin film electrode was also prepared by immersing copper foil in an aqueous solution of  $\text{Na}_2\text{S}$ . The film formed was presumed to be a mixture of  $\text{CuS}$ ,  $\text{Cu}_2\text{S}$ , and  $\text{Cu}_{1.8}\text{S}$ . This thin film electrode was discharged at 1  $\text{ma}/\text{cm}^2$  in an N-phenyl-N,N,N-trimethylammonium hexafluorophosphate-dimethylformamide electrolyte vs. lithium. The amount of active material present was only sufficient for a 1.2 to 1.6 minute discharge. Thus, the results of the test did not provide for an adequate evaluation of the copper sulfide thin film since most of the discharge took place at voltages ascribed to reduction of the electrolyte. Linearly varying potential studies of this cathode are discussed in section B.3.a.

c. Pressed Inorganic Cathodes.

Twenty-eight cathodes were fabricated this quarter from a variety of combinations of inorganic materials with conductive additives and binders. The active cathode materials included  $\text{CuF}_2$ ,  $\text{CoF}_3$ ,  $\text{NiF}_2$ ,  $\text{SbF}_3$ ,  $\text{TiF}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{NiO}$ ,  $\text{AgO}$ ,  $\text{Cu}_2\text{S}$ , and  $\text{CuS}$ .

Six  $\text{CuF}_2$  cathodes were prepared according to the filter pad technique described in the Fifth Quarterly Report. However, smaller amounts of the cathode mix were pressed at higher pressures in order to produce thinner cathodes with less internal resistance. These thin cupric fluoride filter pad cathodes did not exhibit any significant improvement in electrochemical performance over the earlier, thicker types. The addition of small amounts of  $\text{LiClO}_4$  or N-phenyl-N,N,N-trimethylammonium hexafluorophosphate,  $(\text{C}_6\text{H}_5)(\text{CH}_3)_3\text{NPF}_6$ , to the cathode mix did not enhance the electrochemical behavior of the filter pad cathodes. It was hoped that inclusion of these solutes in the electrodes would increase porosity and active surface as they made contact with the electrolyte and dissolved. The data for the half-cell screening of  $\text{CuF}_2$  filter pad cathodes is presented in Table IV, pages IV-6 through IV-19, No. 1 through No. 6.

It was postulated that although the use of thin electrodes might decrease internal resistance losses, the pressures applied to the electrodes could possibly be decreasing their porosity and forming an impenetrable surface layer. In order to substantiate this hypothesis, a thin cupric fluoride cathode in a  $(\text{C}_6\text{H}_5)(\text{CH}_3)_3\text{NPF}_6$ -DMF electrolyte vs. a lithium anode was subjected to a  $50 \text{ ma/cm}^2$  discharge for 30 seconds before testing. It was hoped that this initial exposure to a high current density would result in an "opening up" of the electrode face. The half-cell was next discharged at  $5 \text{ ma/cm}^2$ . The initial  $50 \text{ ma/cm}^2$  load apparently did not achieve the desired effect since the cathode voltage

(vs. Ag/AgCl) had dropped to -1.16V from an open circuit value of -0.04V after one minute at the 5 ma/cm<sup>2</sup> discharge level. However, during an 18 minute discharge, the cathode voltage gradually improved to a value of -0.74V. The electrode was placed on open circuit for one hour and discharged again at 5 ma/cm<sup>2</sup> for 30 minutes. During this discharge, voltage steadily decreased from an initial voltage of -0.18V to -1.59V. At this point, it was decided to determine the effect of a charging operation on the electrode. After charging at 5 ma/cm<sup>2</sup> for 30 minutes, the cell was again discharged at 5 ma/cm<sup>2</sup>. During this final discharge, initial cathode performance was better than during the 30 minute discharge, but the cathode voltage had dropped from an initial value of +0.5V to -1.00V after 12 minutes. Below are listed selected voltage readings taken during the discharges to illustrate the effect of the initial 50 ma/cm<sup>2</sup> discharge and the effect of charging the half-cell:

Cathode Voltage vs. Ag/AgCl During 5 ma/cm<sup>2</sup> Discharge

<u>Time (Minutes)</u>	<u>After 30 Seconds at 50 ma/cm<sup>2</sup></u>	<u>After One Hour On Open Circuit</u>	<u>After Charging</u>
0	-0.30	-0.18	+0.50
1	-1.16	-0.66	-0.03
2	-1.33	-0.95	-0.06
3	-1.39	-1.11	-0.09
4	-1.43	-1.20	-0.12
5	-1.44	-1.27	---
10	-0.82	-1.42	-0.67
14	-0.74	-1.51	-1.24
18	-0.74	-1.57	-1.50
30	---	-1.59	---

Cupric fluoride electrodes were also prepared from various dry mixes. (In the filter pad method cited above, the mix is prepared in a heptane slurry.) Conductive additives and metal substrates

were varied to determine their effect on the electrochemical behavior of  $\text{CuF}_2$ .  $\text{CuF}_2$  cathodes containing acetylene black as the conductive additive and a Solka-Floc binder gave better performance than the filter pad cathodes. However, this might be attributed to the change of electrolyte to  $\text{LiClO}_4$ -propylene carbonate (PC) from a  $(\text{C}_6\text{H}_5)(\text{CH}_3)_3\text{NPF}_6$ -dimethylformamide (DMF) electrolyte which was used to screen all but one of the filter pad electrodes. One electrode composed of  $\text{CuF}_2$  (78 wt. %), acetylene black (11 wt. %), and Solka-Floc (11 wt. %) could sustain discharges of at least  $25 \text{ ma/cm}^2$  without polarizing more negative than -1V. (See No. 7, Table IV, pages IV-6 through IV-19.)

$\text{CuF}_2$  electrodes containing 5 wt. % Cu reached more negative voltages at lower current densities than those containing acetylene black. The two electrodes prepared in this way (No. 12 and No. 13, Table IV, pages IV-6 through IV-19) could sustain a discharge of  $5 \text{ ma/cm}^2$  before reaching voltages more negative than -1.0V.

Silver was also employed as a conductive additive. The Ag was introduced into the cathode by igniting a pellet containing  $\text{CuF}_2$ , AgO, and Solka-Floc. Since AgO decomposes at  $100^\circ\text{C}$  to form Ag and  $\text{O}_2$ , it was hoped that the  $\text{CuF}_2$  would become intimately mixed with Ag and also with carbon from the ignited Solka-Floc. However, decomposition of  $\text{CuF}_2$  may have simultaneously occurred. For the results of the half-cell screening of these cathodes, see No. 25 and No. 26, Table IV, pages IV-6 through IV-19.

Antimony trifluoride was added to three  $\text{CuF}_2$  electrodes. A cathode containing  $\text{CuF}_2$  (70 wt. %),  $\text{SbF}_3$  (10 wt. %), acetylene black (10 wt. %), and Solka-Floc (10 wt. %) could sustain discharges of  $15 \text{ ma/cm}^2$  before polarizing to -1.0V. A linearly

varying potential study of another  $\text{CuF}_2\text{-SbF}_3$  electrode containing no acetylene black proved it capable of sustaining at least  $50 \text{ ma/cm}^2$  without excessive polarization. The data for these cathodes is presented in Table IV, pages IV-6 through IV-19, No. 13 through No. 15.

Although silver, nickel, and copper substrates were used for the  $\text{CuF}_2$  electrodes, a comparison of their relative performance was not made because of variations in composition and mode of fabrication in these initial studies.

Of the cathodes fabricated from inorganic compounds other than  $\text{CuF}_2$ , only two showed any significant output. A copper sulfide cathode prepared by igniting a mixture of  $\text{Cu}_2\text{S}$  (49 wt. %),  $\text{AgO}$  (24 wt. %),  $\text{Cu}$  (16 wt. %),  $\text{S}$  (9 wt. %),  $\text{C}$  (1 wt. %), and Solka-Floc (1 wt. %) could sustain a discharge of at least  $5 \text{ ma/cm}^2$  before reaching voltages more negative than  $-1.0\text{V}$ . The second cathode consisted of  $\text{AgO}$  (85.5 wt. %),  $\text{SbF}_3$  (10 wt. %), and Solka-Floc (4.5 wt. %). Linearly varying potential scans showed that this electrode could sustain at least  $10 \text{ ma/cm}^2$  before polarizing excessively.

In addition to half-cell screening tests, full cell discharges and linearly varying potential studies were used to evaluate pressed inorganic cathodes. A copper sulfide ( $\text{CuS}$ ) electrode and an iron oxide ( $\text{Fe}_3\text{O}_4$ ) electrode were studied in full cell discharges. Both cathodes were prepared from a mixture of 85 wt. % active material, 10 wt. % Dixon graphite, and 5 wt. % Solka-Floc. They were tested in  $(\text{C}_6\text{H}_5)(\text{CH}_3)_3\text{NPF}_6\text{-DMF}$  electrolytes using a lithium anode. As can be seen from the data listed below, both electrodes performed similarly, polarizing rapidly from the open circuit voltage, and maintaining steady voltages on discharge. These voltages seemed to represent a reduction



of some component of the electrolyte rather than of the active cathode material.

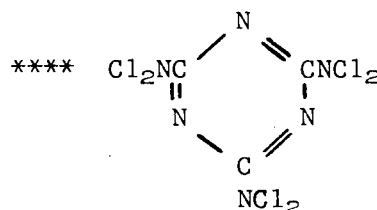
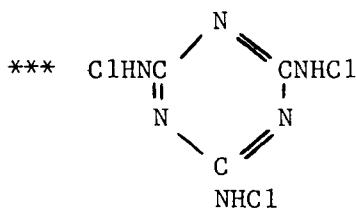
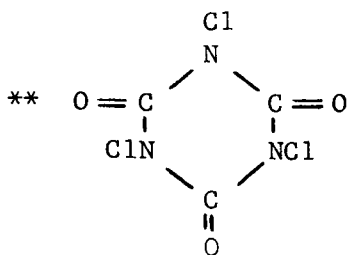
CuS				Fe <sub>3</sub> O <sub>4</sub>			
Time (Hrs.)	Cell Voltage	Cathode Voltage vs. Ag/AgCl	Current Density (ma)	Time (Hrs.)	Cell Voltage	Cathode Voltage vs. Cu	Current Density (ma/cm <sup>2</sup> )
0	3.5	+0.34	0	0	3.07	+0.5	0
0	3.0	Rapidly Polarized to -1.0V	10.2	0	0.9	-1.4	11.0
1	1.4	-1.4	10.2	1	0.9	-1.4	11.0
5	1.0	-1.8	9.2	4	0.7	-1.4	11.0
10	1.0	-1.8	9.5	5	0.4	-1.5	*25.0
15	0.9	-1.8	9.5	5-1/2	0.2	-1.6	*38.0
18	0.8	-1.8	9.4				

Coulombic efficiency studies of pressed inorganic cathodes are discussed in section B.2.a. and linearly varying potential scans are described in section B.3.a.

d. Dissolved Active Organic Cathode Materials.

The investigation of organic compounds for use as cathodes in soluble form was continued this quarter. Electrochemical half-cell screening tests were carried out on m-dinitrobenzene (MDB) and three positive halogen compounds, trichloroisocyanuric acid\*\* (ACL-85), trichloromelamine\*\*\* (TCM), and hexachloromelamine\*\*\*\* (HCM). The trichloroisocyanuric acid was supplied by Monsanto Research Corp. and is designated by them as ACL-85.

\* Current density was increased by adjusting the variable resistor apparatus.



HP-10 Speer carbon working electrodes were used in all but two of the tests. It was observed that the working electrodes often became covered with a film during discharge. In some of the tests, working electrodes were replaced when film formation occurred. This often resulted in a return to initial cathode open circuit voltages.

Lithium counter electrodes were used for the initial half-cell tests this quarter. However, since no form of separation was used to prevent attack of the counter electrode by the active organic material, later tests were conducted with inert HP-10 Speer carbon counter electrodes. It is interesting to note that lithium was reasonably stable for the duration of the test (approximately six hours) in many of the dissolved cathode-electrolyte systems, namely, 1 molal solutions of ACL-85 in  $\text{AlCl}_3$ -acetonitrile\* (AN), 1 molal solutions of ACL-85 and TCM in  $\text{LiPF}_6$ -dimethylformamide (DMF), and 0.1 molal solutions of HCM in  $\text{LiPF}_6$ -DMF.

Ag/AgCl reference electrodes were used in most of the half-cell tests. They were replaced if they appeared to deteriorate during the test. Ag reference electrodes were used in solutions in which Ag/AgCl was extremely unstable. Figure 1e, page IV-25, illustrates the effect of using a Ag reference electrode rather than a Ag/AgCl electrode. The discharge curve for 1 molal ACL-85 contains fewer variations when a Ag reference electrode is employed.

The results of the half-cell screening of dissolved active organic cathode materials using HP-10 Speer carbon working electrodes are summarized below. Further details and graphs of cathode voltage vs. current density can be found in Figure 1, pages IV-20 through IV-32.

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\* Earlier results have shown lithium to be extremely unstable in pure acetonitrile; therefore, some form of corrosion inhibition may be taking place in this solution.

<u>Active Cathode Material</u>	<u>Electrolyte (1 molal)</u>	<u>Current Density Which Could Be Maintained Before The Cathode Voltage Became More Negative Than -1.0V</u>
<u>A. Systems in Which HP-10 Speer Carbon Served as the Counter Electrode</u>		
1. 0.1 m MDB	LiPF <sub>6</sub> -DMF	2.5 ma/cm <sup>2</sup>
2. 1.0 m MDB	LiPF <sub>6</sub> -DMF	2.5 ma/cm <sup>2</sup>
3. 0.1 m ACL-85	LiPF <sub>6</sub> -DMF	2.5 ma/cm <sup>2</sup>
4. 1.0 m ACL-85	LiPF <sub>6</sub> -DMF	20, 40* ma/cm <sup>2</sup>
5. 0.1 m TCM	LiPF <sub>6</sub> -DMF	5 ma/cm <sup>2</sup>
6. 1.0 m TCM	LiPF <sub>6</sub> -DMF	10 ma/cm <sup>2</sup>
7. 0.1 m TCM	LiPF <sub>6</sub> -NDA	0.5 ma/cm <sup>2</sup>
8. 0.1 m HCM	LiPF <sub>6</sub> -DMF	15 ma/cm <sup>2</sup>
9. 1.0 m HCM	LiPF <sub>6</sub> -DMF	20 ma/cm <sup>2</sup>
<u>B. Systems in Which Lithium Served as the Counter Electrode</u>		
1. 0.1 m ACL-85	AlCl <sub>3</sub> -AN	5 ma/cm <sup>2</sup>
2. 1.0 m ACL-85	AlCl <sub>3</sub> -AN	1 ma/cm <sup>2</sup>
3. 0.1 m ACL-85	LiPF <sub>6</sub> -DMF	10 ma/cm <sup>2</sup>
4. 1.0 m ACL-85	LiPF <sub>6</sub> -DMF	10 ma/cm <sup>2</sup>
5. 1.0 m TCM gel**	LiPF <sub>6</sub> -DMF	10, 20, 5 ma/cm <sup>2</sup> ***
6. 0.1 m HCM	LiPF <sub>6</sub> -DMF	40 ma/cm <sup>2</sup>
7. 1.0 m HCM	LiPF <sub>6</sub> -DMF	80 ma/cm <sup>2</sup>

In most cases, the electrochemical performance of these organic cathodes was at least equivalent to that of inorganic cathodes which have been tested. HCM, which could sustain a discharge of 80 ma/cm<sup>2</sup> vs. lithium at a 1 molal concentration in LiPF<sub>6</sub>-DMF without excessive polarization, exceeded the capabilities of any inorganic compound tested thus far.

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\* Values are for systems with Ag and Ag/AgCl reference electrodes, respectively.

\*\* When 1 molal LiPF<sub>6</sub>-DMF was made 1 molal in TCM, within several days the entire solution reacted to form a gelatinous substance. It was found that the electrochemical activity of this gel decreased on standing.

\*\*\* Values are for systems with HP-10 Speer carbon, Cu, and Ag working electrodes, respectively.

Because of their low equivalent weights, high open circuit voltages, and ability to maintain substantial current densities, the organic cathode materials will be investigated further. Modifications in the testing procedure may include the use of non-porous carbon electrodes to assure reproducibility of results, the use of Ag rather than Ag/AgCl reference electrodes, and the utilization of separator materials to prevent migration of the active organic material to the anode.

Density and viscosity measurements were made for a number of the dissolved active organic materials before and after discharge. If high molecular weight products are formed in the electrochemical reaction, they should cause an increase in viscosity and density of the solution. An increase in viscosity was indeed noted in seven of the ten half-cells. However, the accuracy of the measurements was limited in a number of the tests because of gas evolution and solid formation in the solution. Density and viscosity data are given in Table V, page IV-33.

Coulombic efficiency studies and linearly varying potential studies of dissolved organic cathode materials are discussed in sections B.2.b. and B.3.b., respectively.

## 2. Coulombic Efficiency Studies.

### a. Inorganic Cathodes.

Coulombic efficiency determinations were carried out this quarter with cupric fluoride filter pad cathodes, sintered cupric fluoride electrodes, and several pressed inorganic cathodes. N-Phenyl-N,N,N-trimethylammonium hexafluorophosphate  $[(C_6H_5)(CH_3)_3NPF_6]$  -dimethylformamide (DMF), LiCl-DMF, and LiClO<sub>4</sub>-propylene carbonate (PC) electrolytes were employed. Lithium anodes and Ag/AgCl reference electrodes were used for all of the tests. All but two of the discharges were allowed to proceed spontaneously through a transistorized variable resistor which automatically adjusted the resistance

to maintain constant current. The two forced discharges are clearly identified in Table VI. Coulombic efficiencies were calculated using a cut-off voltage of 0.2V for the cell.

Two cupric fluoride filter pad cathodes discharged at 1.79 and 9.2 ma in  $(C_6H_5)(CH_3)_3NPF_6$ -DMF yielded efficiencies of 144.6% and 191.3% respectively. These efficiencies in excess of 100% are ascribed to the reduction of some component of the electrolyte which contributes to the total number of coulombs obtained. This is substantiated by the linearly varying potential (LVP) scans of various electrolytes depicted in Figure 6, page IV-82, and by the plots of cathode voltage vs. per cent theoretical coulombs in Figures 2a and 2b, pages IV-42 and IV-43. A major portion of the discharges shown in Figure 2 occur at voltages where electrolyte reduction can take place as demonstrated by the LVP scans in Figure 6c, page IV-84.

All coulombic efficiency studies of sintered  $CuF_2$  electrodes this quarter were made using  $LiClO_4$ -PC electrolytes. Sintered  $CuF_2$  electrodes prepared in a tube furnace purged with nitrogen yielded efficiencies ranging from 35.3% to 54.5% when discharged at approximately 2 ma. Similar electrodes discharged at approximately 10 ma yielded efficiencies of 18.3 and 31.7%.

The coulombic efficiencies of sintered  $CuF_2$  electrodes prepared in a metallurgical press (hot pressed) ranged from 14.8% to 58.7% for 2 ma discharges. At approximately 10 ma, electrodes prepared in the same manner yielded efficiencies of 3.4% to 28.2%. In testing the sintered  $CuF_2$  cathodes prepared in a metallurgical press, several variations were introduced. These variables are given below:

1. Use of a minimal amount of electrolyte (approximately 2-3 ml) rather than 25-30 ml.

2. Vacuum and nitrogen-drying\* the  $\text{CuF}_2$  prior to sintering.
3. Forcing the cell to discharge at a given current rather than allowing it to proceed spontaneously through a transistorized variable resistor.
4. Varying the substrate metal.

Coulombic efficiency calculations were also made for several pressed inorganic cathodes. A nickel hydroxide electrode discharged in  $\text{LiClO}_4\text{-PC}$  at  $1.5 \text{ ma/cm}^2$  gave 21.4% utilization of the active material.

A silver oxide cathode discharged at  $1.79 \text{ ma/cm}^2$  in  $(\text{C}_6\text{H}_5)(\text{CH}_3)_3\text{-NPF}_6\text{-DMF}$  yielded an efficiency of 168.7%. When the test was repeated using a filter paper separator between the anolyte and catholyte, the coulombic efficiency was 117.7%. The reduction of some component of the electrolyte has been postulated as being the cause of efficiencies in excess of 100%. A silver oxide cathode discharged in  $\text{LiClO}_4\text{-PC}$ , again with a filter paper separator, polarized rapidly at 1 and  $5 \text{ ma/cm}^2$ . A coulombic efficiency calculation was not attempted for this cell.

Two vanadium pentoxide cathodes were tested in  $\text{LiClO}_4\text{-PC}$  at 1.3 and  $5 \text{ ma/cm}^2$ . The electrode discharged at  $1.3 \text{ ma/cm}^2$  was 68.1% efficient based on a one electron change per vanadium atom. The second vanadium pentoxide electrode yielded an efficiency of 1.1%.

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\* The method of drying was similar to that described on page 2 for  $\text{LiPF}_6$ . The  $\text{CuF}_2$  was nitrogen-dried at  $130^\circ\text{C}$  for 18 hours.

The data for the coulombic efficiency tests are presented in Table VI, pages IV-34 through IV-41. Plots of cathode voltage and cell voltage vs. per cent theoretical coulombs are depicted in Figure 2, pages IV-42 through IV-59, for a number of the tests in Table VI.

b. Dissolved Active Organic Cathodes.

Coulombic efficiency determinations were made for m-dinitrobenzene\* (MDB) and trichloroisocyanuric acid (ACL-85)\*\* using lithium anodes and HP-10 Speer carbon working electrodes. Calculations were based on a cut-off cell voltage of 0.2V. A one molal solution of MDB in 1 molal  $\text{LiPF}_6$ (undried)-dimethylformamide yielded an efficiency of less than 1% at an average current density of 1.6 ma/cm<sup>2</sup>.

ACL-85 at a concentration of 0.01 molal in 1 molal  $\text{LiPF}_6$ (dried)-N-nitrosodimethylamine (NDA) gave efficiencies of 11.7% and 70.0% at average currents of 10.2 and 1.9 ma\*\*\* respectively. Both cells were operated under forced discharge conditions. Plots of cathode voltage and cell voltage vs. per cent theoretical coulombs for the ACL-85- $\text{LiPF}_6$ -NDA cells are depicted in Figure 3, page IV-60.

3. Linearly Varying Potential Studies.

a. Inorganic Cathodes.

Linearly varying potential studies were made of sintered cupric fluoride cathodes, thin film cathodes, and pressed inorganic cathodes.

Linearly varying potential scans of cupric fluoride sintered on copper foil, copper screen, and aluminum and silver expanded metal are depicted in Figure 4a, page IV-62. These electrodes were prepared by clamping the samples in a die and heating the die in a nitrogen-purged tube furnace. (A detailed description of this method of sintering is presented on page 4.)  $\text{LiClO}_4$ -propylene

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\* The coulombic efficiency calculation was based on a 12 electron reaction.

\*\* The coulombic efficiency calculation was based on a 6 electron reaction.

\*\*\* Approximately 5 and 1 ma/cm<sup>2</sup>, respectively.

carbonate (PC) electrolytes (1 molal) were employed. The higher currents supported by the Cu screen and Ag expanded metal are probably due to the presence of more active material on these relatively open substrates. The Al substrate values are lower than might be expected on a similar basis; however, if a film of aluminum oxide were present on the surface of the substrate, the internal resistance drop would be high, thereby lowering the observed current. The double wave appearing in the Cu foil scan is of interest since the only difference between this sample and the other three is the substrate. The doublet is indicative of more than one electron transfer step taking place.

The initial anodic currents observed in these scans may create changes in the surface which interfere with the reactions causing the cathodic currents. For this reason, later scans of sintered cupric fluoride electrodes were made with the initial potential set equal to the open circuit voltage of the cathode half-cell. In this way, the initial anodic currents were eliminated and interference with cathodic reactions was avoided.

Using this modification in the linearly varying potential technique, cupric fluoride sintered on aluminum was scanned again. (See Figure 4b, page IV-63.) The cathodic current in the 0 to -1.0V range was decreased from the values in Figure 4a when the scans were started at the initial open circuit potential. The lower currents in this range may have resulted from the elimination of oxidation reactions which might take place when the scans are started at more positive voltages. If oxidation of some substance occurred, its subsequent reduction would enhance the cathodic current.

In Figure 4c, page IV-64, linearly varying potential scans of cupric fluoride sintered on silver expanded metal in a metallurgical press are depicted. Several reduction waves are evident



and cathodic currents are considerably higher than in Figures 4a and 4b. It should be noted that a  $\text{LiPF}_6$ -N-nitrosodimethylamine (NDA) electrolyte (1 molal) was used in this test rather than the  $\text{LiClO}_4$ -PC electrolyte used for the earlier studies. Linearly varying potential studies of  $\text{LiPF}_6$ -NDA will have to be made in order to make a complete evaluation of this system.

Cupric fluoride thin films formed on copper foil by solvent evaporation and electrodeposition were evaluated by the linearly varying potential technique. Copper oxides (I and II) produced during the electrolysis were also studied. (See pages 6 and 7 for details of fabrication.) No distinctive features are present in the scans of cupric fluoride thin films depicted in Figure 4d, page IV-65. Comparison with the curves for  $\text{LiClO}_4$ -PC and copper foil electrodes in Figure 6a, page IV-82, indicate that the current from the small amount of cupric fluoride present may be obscured. The scans of copper oxides are presented in Figure 4e, page IV-66, for comparison with the scans of cupric fluoride thin films. Examination of the cupric fluoride curves in Figure 4d, page IV-65, indicates a strong possibility that a copper oxide is being reduced.

Linearly varying potential studies were carried out on a thin film of copper sulfide on copper foil. (See page 7 for details of fabrication.) An N-phenyl-N,N,N-trimethylammonium hexafluorophosphate-dimethylformamide electrolyte was employed. Several of the voltage scans are depicted in Figure 4f, page IV-67. The initial scan shows a large reduction wave at about -0.2V with only a hint of a second reduction at more negative voltages. Very little oxidation is evident in the reverse scan. As the potential range examined was broadened and more scans were run, definite changes in reactions took place as illustrated by scans 5 and 9 in Figure 4f, page IV-67. Several reduction waves are now present. These all seem relatively reversible as evidenced by oxidation waves at

similar potentials. Thus, reduction at a copper sulfide electrode after the initial scan appears to involve complex interactions with the electrolyte.

Linearly varying potential studies of pressed inorganic cathodes are depicted in Figures 4g to 4i, pages IV-68 through IV-71. The electrochemical characteristics of antimony trifluoride and cupric fluoride and silver oxide combined with antimony trifluoride were investigated.  $\text{LiClO}_4$ -PC electrolytes were used. As can be seen in Figure 4g, pages IV-68 and IV-69, the addition of carbon and a Solka-Floc binder to antimony trifluoride increases cathodic currents considerably. The use of silver rather than nickel as the substrate metal also seems to improve electrochemical performance. The curves for antimony trifluoride exhibit no distinctive reduction waves, possibly because of the large resistance encountered with pellet-type cathodes.

Figure 4h, page IV-70, illustrates the effect of adding a small amount of antimony trifluoride to a cupric fluoride electrode. A cupric fluoride electrode containing 10 wt. %  $\text{SbF}_3$  produced significantly higher cathodic currents than a similar cathode containing a carbon additive in place of the  $\text{SbF}_3$ .

The linearly varying potential scan of a silver oxide cathode containing 10 wt. % antimony trifluoride in Figure 4i, page IV-71, contains no distinctive features other than a reduction wave which is beginning to appear as -2.0V is approached.

b. Dissolved Active Organic Cathodes.

Studies were made of N-chlorosuccinimide and 2,4-dinitrophenol at two concentrations in a one molal  $\text{LiPF}_6$ -dimethylformamide electrolyte. The results of these tests are shown in Figures 5a and 5b, pages IV-73 and IV-74, respectively. The expected increase in current with increasing concentration was found for N-chlorosuccinimide. However, it is interesting to note that, over the voltage range examined, the 2,4-dinitrophenol shows very

little dependence upon concentration. Thus, it may be postulated that the reduction of 2,4-dinitrophenol proceeds through a concentration independent step in the voltage range studied.

Linearly varying potential scans of the positive halogen compounds, trichloroisocyanuric acid (ACL-85), trichloromelamine (TCM), and hexachloromelamine (HCM) are shown in Figures 5c through 5h on pages IV-75 to IV-80. The high currents obtained in half-cell screening tests for these compounds are also present in these scans. Studies were made of the gelled material formed by the reaction of TCM with the one molal  $\text{LiPF}_6$ -dimethylformamide (DMF) electrolyte and of a saturated ( $<1$  molal) solution of TCM in one molal  $\text{LiClO}_4$ -propylene carbonate. Typical curves for these systems are shown in Figures 5d and 5e, pages IV-76 and IV-77. In addition, a comparison of the initial scan in each electrolyte is given in Figure 5f, page IV-78.

Figure 5g, page IV-79, gives a comparison of TCM at two different concentrations in 1 molal  $\text{LiPF}_6$ -DMF. There is no marked difference in the two curves, although the increase in current is less than one would expect with a ten-fold increase in concentration.

### C. Electrolytes.

#### 1. Distillation and Characterization of Solvents Employed in Electrolytic Solutions.

Twelve week tests for N-nitrosodimethylamine (NDA), distilled according to the method described in previous reports, have been completed. These tests include the measurement of refractive index and specific conductivity of the various fractions, which are stored in a dry argon atmosphere between tests. It was found that the refractive index of undistilled NDA differed from the indices of the distilled fractions, initially and after 12 weeks. Differences in specific conductivity were not significant and comparison is difficult because

the measurements are being made at the lower limits of the conductivity bridge. The refractive indices of the distilled fractions remained virtually constant during the twelve week period. Specific conductivities showed a slight increase. The data for the twelve week tests are given in Table VII, page IV-81.

## 2. Treatment With Inhibitors.

Experimentation has shown that lithium is considerably more stable in N-phenyl-N,N,N-trimethylammonium hexafluorophosphate-dimethylformamide (DMF) solutions than in DMF alone. This has led to the hypothesis that a substituted amine might possibly be useful as a corrosion inhibitor.

During this reporting period, one tertiary amine, tri-n-propylamine (TPA), was tested for ability to prevent corrosion of Li by DMF. A piece of lithium in DMF was completely consumed in 16 hours, leaving a yellow-orange gelatinous precipitate. Lithium in TPA turned black and gassed for 8 hours but no further change occurred. When a one molal solution of TPA in DMF was prepared, two liquid phases were formed. A piece of lithium floating in the TPA layer became covered with a white solid but no appreciable consumption occurred. A gelatinous precipitate similar to the one formed in pure DMF was produced in the DMF layer. When a piece of lithium was placed in DMF saturated with TPA, a large amount of precipitate was formed but the metal did not appear to be completely consumed. Therefore, it can be concluded that TPA does, to some extent, inhibit lithium consumption by DMF.

## 3. Stability of Anode Materials in Electrolytic Solutions.

Stability tests of two weeks duration were made for lithium and calcium in electrolytes which had been pretreated with the same metals. Half-cell screening of anode metals in pretreated electrolytes was described in previous reports. These tests had indicated that pretreated electrolytes might prevent anode corrosion

by the electrolyte without significantly decreasing the ability of the systems to sustain high current densities.

Lithium and calcium strips were placed in Li and Ca pretreated solutions (1 molal) of morpholinium hexafluorophosphate in dimethylformamide and N-nitrosodimethylamine (NDA). Lithium in pretreated morpholinium hexafluorophosphate-NDA was the only stable system.

#### 4. Linearly Varying Potential Studies of Electrolyte Decomposition.

In view of the coulombic efficiencies in excess of 100% obtained with some cathodes in N-phenyl-N,N,N-trimethylammonium hexafluorophosphate-dimethylformamide electrolytes, a study was made to determine whether some component of the electrolyte might be contributing to coulombic output. In these coulombic efficiency tests, a reduction plateau occurs in the -1.5 to -2.0V range. Linearly varying potential scans were made of a series of electrolytes to determine whether or not this plateau could be attributed to electrolyte reduction.

Linearly varying potential scans were made of  $\text{LiClO}_4$ -propylene carbonate (PC),  $\text{LiCl}$ -dimethylformamide (DMF), and N-phenyl-N,N,N-trimethylammonium hexafluorophosphate-DMF using carbon, copper, and silver working electrodes. The scans are depicted in Figure 6, pages IV-82 through IV-84. The scans made with Cu working electrodes were not definitive. They were complicated by the presence of reduction waves in the 0 to -1V range which might possibly be attributed to copper oxides formed at more positive voltages. The linearly varying potential scans made with Speer carbon working electrodes show reductions occurring in the -1.5 to -2.0V range for the DMF electrolytes. This does not occur in the  $\text{LiClO}_4$ -PC system. A linearly varying potential scan of  $\text{LiClO}_4$ -PC made with a Ag working electrode shows very little reduction taking place at voltages as negative as -3.0V. These studies substantiate the hypothesis that DMF is being reduced during full cell discharges.

D. Components.

1. Separators.

Three types of separators, anion exchange membranes, filter paper, and an epoxy membrane, were tested under full cell conditions during the sixth quarter. The method of evaluating the separator materials was as follows. A polypropylene cell containing two 1x1x1 cm wells separated by a 1 cm<sup>2</sup> piece of the membrane was used for the tests. The anode and cathode or cathodic current collector were placed against the cell walls at a distance of 1 cm from either side of the membrane. Reference electrodes, masked with tape on one side, were placed in the anolyte and the catholyte. They were located as close to the membrane as possible to allow for an accurate measurement of the potential drop across the membrane. The tape prevented contact of the reference electrode with the membrane. The voltage readings of anode reference electrode vs. cathode reference electrode in Table VIII, pages IV-85 through IV-93, are indicative of the drop in potential occurring across the membrane. Current was gradually increased through a transistorized variable resistor to the maximum amount which the cell could maintain and was then decreased in the same manner to 0 ma. The cells were then allowed to discharge at maximum current so that a sufficient amount of reaction products would be formed for X-ray analysis.

The results for the full cell testing of the three separator materials are described below.

a. Anion Exchange Membranes.

The testing of an anion exchange membrane (E-5451-1/2, Ionics, Inc.) using a Li-CuCl<sub>2</sub>·2H<sub>2</sub>O couple was repeated during the sixth quarter. The CuCl<sub>2</sub>·2H<sub>2</sub>O was dissolved in an N-phenyl-N,N,N-trimethylammonium hexafluorophosphate-dimethylformamide (DMF) electrolyte. In the original test, described in the Fifth Quarterly Report (page IV-73), leakage of CuCl<sub>2</sub>·2H<sub>2</sub>O into the anolyte was visually apparent. The test was repeated to determine

whether leakage had occurred because of poor mechanical construction or through the membrane itself. No leakage occurred in the second experiment. The anion exchange membrane proved unsatisfactory. The potential drop across the membrane during a 5 ma discharge exceeded 2V causing cell voltage to approach 0V.

A fuel cell membrane (E-7083, Ionics, Inc.) equilibrated in DMF was received during this quarter. Previous anion exchange membrane samples were equilibrated in water and had to be re-equilibrated in the electrolyte solvent, whereas this membrane could be used "as received." The DMF-equilibrated fuel cell membrane exhibited only slightly improved performance over the E-5451-1/2 membrane under the same test conditions. The potential drop across the membrane was 1.83V at a maximum current of 7.1 ma. X-ray diffraction analysis of the anode showed that copper deposition had occurred on that electrode.

The DMF-equilibrated membrane was re-equilibrated in N-nitrosodimethylamine (NDA) and was tested in a cell consisting of a lithium anode,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  dissolved cathode, and N-phenyl-N,N,N-trimethylammonium hexafluorophosphate-NDA electrolyte. The loss in voltage occurring across the membrane was  $< 0.5\text{V}$  in this cell. However, overall cell performance was poor and the copper current collector was attacked by Ag ions presumably introduced into the solution from the Ag/AgCl reference electrode. X-ray diffraction analysis did not conclusively show whether the membrane had achieved separation of anolyte and catholyte. The results of the full cell testing with the fuel cell ion exchange membrane are given in Table VIII, pages IV-86 through IV-89.

b. Filter Paper.

A cell consisting of a lithium anode, AgO cathode, and N-phenyl-N,N,N-trimethylammonium hexafluorophosphate-DMF electrolyte was discharged with a No. 40 Whatman filter paper separator. The

drop in potential across the membrane was  $< 1V$  at currents as great as 20 ma. The results for the above test are given in Table VIII, pages IV-90 and IV-91.

c. Epoxy Membrane.

The separating capabilities of a Versapor epoxy membrane, No. 6429 (Gelman), were evaluated using a trichloroisocyanuric acid (ACL-85) soluble cathode. A lithium anode, an inert carbon cathode current collector, and  $LiPF_6$ -dimethylformamide electrolyte were employed. The membrane was stable in this system and X-ray diffraction analysis gave no evidence for attack of the lithium anode by the active cathode material. The maximum loss in potential across the membrane was  $0.81V$  at 7 ma. However, overall cell performance was poor due to cathode polarization of  $> 1V$  at low current densities.

The experimental details for the testing of the Versapor epoxy membrane are given in Table VIII, pages IV-92 and IV-93. The separating characteristics of this membrane will have to be tested using another soluble cathode, possibly  $CuCl_2 \cdot 2H_2O$ , before an adequate evaluation can be made.

2. Case Materials.

A study of the stability of possible case materials in various electrolytes has been initiated. Polyethylene and polypropylene were tested for two weeks in electrolytes prepared from  $NH_4PF_6$ , morpholinium hexafluorophosphate ( $O \begin{smallmatrix} CH_2CH_2 \\ CH_2CH_2 \end{smallmatrix} NH_2PF_6$ ), and  $(C_6H_5)(CH_3)_3NPF_6$  in NDA and DMF. The two materials were stable in the pure solvents and the electrolytes over the two week period. The results of these tests are presented in Table IX, page IV-94.



## II. CURRENT PROBLEMS

## II. CURRENT PROBLEMS

The major problem continues to be that of developing a cathode with suitable characteristics for a high energy density battery.

III. WORK TO BE PERFORMED

### III. WORK TO BE PERFORMED

#### A. During the Next Quarter.

##### 1. Anodes.

Although the anode half-cell screening program is essentially complete, exceptions will be made for promising anode-electrolyte combinations. Because of the recent investigation of dissolved organic cathode materials, the stability of anode metals in these systems will be determined.

##### 2. Cathodes.

Fabrication and electrochemical testing of sintered (hot-pressed) and pressed inorganic cathodes will be continued. The investigation of dissolved active organic cathodes will also be continued. The solubility of these compounds in various electrolytes will be determined. If any cases of limited solubility are found, the use of a pressed, pellet-type organic electrode in a solution saturated with the same organic compound may be possible. This would eliminate the diffusion limitations exhibited in the soluble cathode-electrolyte systems.

Linearly varying potential studies and coulombic efficiency determinations will continue to be made for promising cathodes.

##### 3. Electrolytes.

Purification and characterization of solvents used in electrolytic solutions will be continued. Further studies will be made of electrolytes which permit higher anode discharge rates. These studies will include measurement of specific conductance, density, and viscosity at 25°C over a wide range of concentrations.

4. Components.

Further testing of separators, particularly when liquid or dissolved cathodes are employed, will be made. Separator materials being investigated include various ion exchange membranes, porous plastics, and filter paper. An investigation of case and lead materials for compatibility with electrolytes will be continued.

5. Batteries.

Systems showing promise in half-cell screening tests will be assembled to yield information on problems associated with construction of complete systems.

B. During the Next Month.

1. Anodes.

The stability of anode metals in the dissolved organic cathode-electrolyte systems will be investigated.

2. Cathodes.

The fabrication and electrochemical testing of sintered cathodes and pressed inorganic cathodes will be continued. Sintered cupric fluoride cathodes containing carbon will be prepared in an effort to improve cathode voltages.

The investigation of dissolved active organic cathodes, particularly the positive halogen compounds, will be continued. The solubility of these compounds in various electrolytes will be determined. If any cases of limited solubility are found, the use of a pressed, pellet-type organic electrode in a solution saturated with the same organic compound may be possible. This would eliminate the diffusion limitations exhibited in the soluble cathode-electrolyte systems.

Linearly varying potential studies and coulombic efficiency studies of inorganic and organic cathode materials will be continued. Several

coulombic efficiency tests will be carried out using a minimal amount of electrolyte in order to approach actual battery conditions.

3. Electrolytes.

The distillation of solvents being used in electrolytic solutions will continue. Characterization of these solvents will be made using a gas chromatograph.

Further studies of electrolyte decomposition will be made using the linearly varying potential technique. Inert, non-porous, pyrolytic graphite electrodes will be employed to assure accurate interpretation of the discharge curves.

4. Components.

Full cell testing of separating materials will be continued.

IV. TEST RESULTS

TABLE I. EFFECT OF DRYING THE SOLUTE ON ELECTROCHEMICAL PERFORMANCE OF LITHIUM ANODES

Electrolyte	Solvent		Solute	Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm <sup>2</sup> )	Voltage of Anode vs. Reference Electrode at Various Current Densities		Further Observations and Remarks
	Solvent	Solute	Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm <sup>2</sup> )	Voltage of Anode vs. Reference Electrode at Various Current Densities			
								Initial	Final		
1.	DMF*	LiPF <sub>6</sub> (undried)	Ag/AgCl	Ag/AgCl	-3.27	-3.27	0.1	-3.26	-3.26	The lithium anode and Ag/AgCl counter electrode began gassing during the 10ma/cm <sup>2</sup> discharge. At the end of the discharges the counter electrode was black.	
						-3.25	1.0	-3.24	-3.22		
						-3.23	5.0	-3.12	-3.06		
						-3.18	10.0	-2.97	-3.05		
						-3.15	20.0	-2.91	-2.97		
						-3.13	50.0	-2.72	-2.82		
2.	DMF	LiPF <sub>6</sub> **	Ag/AgCl	Ag/AgCl	-3.25	-3.2	0.1	-3.2	-3.2	During the 5ma/cm <sup>2</sup> discharge a solid formed on the lithium anode.	
						-3.05	1.0	-3.05	-3.0		
						-3.2	5.0	-2.25	-0.9		
3.	DMF	LiPF <sub>6</sub> ***	Ag/AgCl	Ag/AgCl	-3.33	-3.24	0.1	-3.30	-3.23	The counter electrode turned black. During the 20ma/cm <sup>2</sup> discharge, two layers formed in the electrolyte.	
						-3.15	1.0	-3.19	-3.08		
						-3.13	5.0	-2.95	-2.87		
						-3.08	10.0	-2.66	-2.63		
						-3.08	20.0	-2.25	-2.00		
						-3.00	50.0	-1.20			

\* Dimethylformamide

\*\* The LiPF<sub>6</sub> was dried for ca. 12 hours at 110°C in a vacuum oven purged with N<sub>2</sub>.\*\*\* The LiPF<sub>6</sub> was dried for ca. 24 hours at 110°C in the apparatus described on page 2.



TABLE I. EFFECT OF DRYING THE SOLUTE ON ELECTROCHEMICAL PERFORMANCE OF LITHIUM ANODES (Continued)

Electrolyte		Counter Electrode	Reference Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm <sup>2</sup> )	Voltage of Anode vs. Reference Electrode at Various Current Densities		Further Observations and Remarks
Solvent	Solute						Initial	Final	
NDA*	LiPF <sub>6</sub> (undried)	Ag/AgCl	Ag/AgCl	-3.33	-3.37	0.1	-3.32	-3.37	Continuous gassing of the Li anode. Slight gassing occurred at the counter electrode during the 100ma/cm <sup>2</sup> discharge. At the end of the discharges the lithium was covered with a gray film.
					-3.36	1.0	-3.36	-3.37	
NDA	LiPF <sub>6</sub> **	Ag/AgCl	Ag/AgCl	-3.45	-2.85	10.0	-3.20	-2.76	
					-2.83	100.0	-1.98	-1.84	
5.		Ag/AgCl	Ag/AgCl	-3.45	-3.45	0.1	-3.45	-3.45	The counter electrode turned black during the discharges.
					-3.45	1.0	-3.43	-3.43	
					-2.93	10.0	-3.25	-3.15	
					-2.98	100.0	-1.82	-1.89	

NOTE: The specific conductances for the electrolytes in No. 1, 3, 4, and 5 were  $2.09 \times 10^{-2}$  (32°C),  $1.90 \times 10^{-2}$  (29°C),  $1.92 \times 10^{-2}$  (26°C), and  $1.92 \times 10^{-2}$  (30°C) ohm<sup>-1</sup> cm<sup>-1</sup> respectively.

\* N-Nitrosodimethylamine.

\*\* The LiPF<sub>6</sub> was dried for ca. 24 hours at 110°C in the apparatus described on page 2.

TABLE II. ELECTROCHEMICAL HALF-CELL SCREENING OF SINTERED CUPRIC FLUORIDE CATHODES

Matrix (0.75" Dia.)*	Sintering Temper- ature	Sintering Time	Electro- lyte (1 molal)	Counter Elec- trode	Time of Measure- ment	Voltage of Cathode vs. Ag/AgCl Reference Electrode at Various Current Densities**(ma/cm <sup>2</sup> ),								
						0	0.02	0.2	0.9	1.8	2.7	3.6	4.5	5.4
1. Cu screen	150°C	2 hrs.	(C <sub>6</sub> H <sub>5</sub> )(CH <sub>3</sub> ) <sub>3</sub> NPF <sub>6</sub> -DMF	Li	Initial Final	-0.08 -0.4	-0.12 -0.20	-0.45 -0.76	-1.2 -1.48	-1.5 -1.7	*** ***	-1.5 -1.95	*** ***	-1.6 -2.08
2. Al ex- panded metal	200°C	2 hrs.	"	"	Initial Final	0 -0.48	-0.53 -0.55	-0.98 -1.3	*** ***	-1.7 -1.87	-1.8 -1.95	-1.9 -2.02 (1 min)	*** ***	*** ***
3. Ag ex- panded metal	200°C	2 hrs.	"	"	Initial Final	-0.25 -0.5	-0.35 -0.4	-0.82 -1.12	-1.3 -1.5	-1.5 -1.78	-1.7 -1.95	-1.8 -2.09 (3 min)	*** ***	*** ***
4. Ni ex- panded metal	200°C	2 hrs.	"	"	Initial Final	-0.3 -0.8	-0.38 -0.43	-0.76 -1.08	-1.26 -1.45	-1.38 -1.71	-1.70 -1.9	-1.85 -1.99	-1.9 -2.05 (3 min)	*** ***

A gray-brown solid formed in the electrolyte during the discharge of No. 4.

\* Area = 2.8cm<sup>2</sup>.

\*\* Duration of discharge at each current density - 5 minutes (unless noted otherwise).

\*\*\* Not run.

TABLE III. PHYSICAL CHARACTERISTICS OF SINTERED CUPRIC FLUORIDE CATHODES  
PREPARED IN A METALLURGICAL PRESS

Test No.	Substrate	Sintering Temperature (°C)	Sintering Time	Pressure (psi)	Treatment of Die Faces	Results *
1.	Ag expanded metal (0.005" thick)	160±5°	5 sec.	17,800	None	The sample was difficult to remove from the die. X-ray diffraction analysis showed partial decomposition to Cu. A trace of CuF <sub>2</sub> ·2H <sub>2</sub> O was also detected.
2.	Ag expanded metal (0.005" thick)	150±5°	60 min.	8,900	Sprayed with Teflon	The use of Teflon spray partially reduced adherence of the sample to the die. Partial decomposition of CuF <sub>2</sub> to Cu was visually apparent.
3.	Ag expanded metal (0.005" thick)	150±5°	30 min.	8,900	Sprayed with Teflon and dried at 120°C for two hours	Drying the Teflon coating on the die faces did not significantly decrease adherence of the sample to the die. Decomposition of CuF <sub>2</sub> to Cu was again visually apparent but to a lesser degree than in Test No. 2.
4.	Ag expanded metal (0.005" thick)	150±5°	15 min.	8,900	Sprayed with Teflon and dried at 120°C for two hours	Partial decomposition of CuF <sub>2</sub> to Cu is still visually apparent.

\* Sintering was achieved in all of the tests.

TABLE III. PHYSICAL CHARACTERISTICS OF SINTERED CUPRIC FLUORIDE CATHODES  
PREPARED IN A METALLURGICAL PRESS

Test No.	Substrate	Sintering Temperature (°C)	Sintering Time	Pressure (psi)	Treatment of Die Faces	Results *
** 5.	Ag expanded metal (0.005" thick)	150±5°	5 sec.	8,900	Sprayed with Teflon and dried at 120°C for two hours	Partial decomposition of CuF <sub>2</sub> to Cu is still visually apparent.
*** 6.	Ag expanded metal (0.005" thick)	150±5°	5 sec.	8,900	Sprayed with Teflon and dried at 120°C for two hours	X-ray diffraction analy- sis indicated that the sample was pure CuF <sub>2</sub> .
*** 7.	Ag expanded metal (0.005" thick)	150±5°	5 sec.	8,900	Covered with Teflon tape (0.002" thick)	The use of Teflon rather than Teflon spray re- sulted in easy removal of the sample from the die. X-ray diffraction analysis indicated that the sample was pure CuF <sub>2</sub> .

\* Sintering was achieved in all of the tests.

\*\* This sample was cooled rapidly by passing an air stream over the die.

\*\*\* This sample was cooled rapidly by means of a conduction cooling jacket.

TABLE IV. ELECTROCHEMICAL HALF-CELL SCREENING  
OF PRESSED INORGANIC CATHODES

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B. Electrochemical Details For Cathodes Evaluated in Five Minute Discharges at Various Current Densities	IV-15
C. Electrochemical Details For Cathodes Evaluated From Linearly Varying Potential Scans	IV-19

TABLE IV. ELECTROCHEMICAL HALF-CELL SCREENING OF PRESSED INORGANIC CATHODES

## A. Physical Details

Active Cathode Material	Composition of Cathode Mix	Matrix	Method of Preparation	Electrolyte (1 molal)	Counter Electrode
1. $\text{CuF}_2$	78 wt. % $\text{CuF}_2$ , 11 wt. % Dixon graphite No. 200-43, 11 wt. % filter paper pulp.	Ag expanded metal	A heptane slurry of the cathode mix was filtered on a Buchner funnel. The resulting porous mat was pressed at 15,000 lb/cm <sup>2</sup> on a 1cm <sup>2</sup> matrix. One side of the electrode was masked with tape. 0.098g of mix were used. The cathode had a thickness of 0.52mm.	$(\text{C}_6\text{H}_5)(\text{CH}_3)_3\text{NPF}_6\text{-DMF}$	Li
2. $\text{CuF}_2$	78 wt. % $\text{CuF}_2$ , 11 wt. % Dixon graphite No. 200-43, 11 wt. % filter paper pulp.	Ag expanded metal	The method of preparation was identical to that given for No. 1.	$(\text{C}_6\text{H}_5)(\text{CH}_3)_3\text{NPF}_6\text{-DMF}$	Li
3. $\text{CuF}_2$	70.2 wt. % $\text{CuF}_2$ , 10.0 wt. % $\text{LiClO}_4$ , 9.9 wt. % Dixon graphite No. 200-43, 9.9 wt. % filter paper pulp.	Ag expanded metal	The method of preparation was identical to that given for No. 1. 0.0513g of mix were used. The cathode had a thickness of 0.285mm.	$\text{LiClO}_4\text{-PC}$	Li
4. $\text{CuF}_2$	The composition was identical to that given for No. 3.	Ag expanded metal	The method of preparation was identical to that given for No. 1. 0.0548g of mix were used. The cathode had a thickness of 0.300mm.	$(\text{C}_6\text{H}_5)(\text{CH}_3)_3\text{NPF}_6\text{-DMF}$	Li

TABLE IV. ELECTROCHEMICAL HALF-CELL SCREENING OF PRESSED INORGANIC CATHODES (Continued)

## A. Physical Details (Continued)

Active Cathode Material	Composition of Cathode Mix	Matrix	Method of Preparation	Electrolyte (1 molal)	Counter Electrode
5. $\text{CuF}_2$	70.2 wt. % $\text{CuF}_2$ , 10.0 wt. % $(\text{C}_6\text{H}_5)(\text{CH}_3)_3\text{NPF}_6$ , 9.9 wt. % Dixon graphite No. 200-43, 9.9 wt. % filter paper pulp.	Ni expanded metal	The method of preparation was identical to that given for No. 1 but the electrode was not masked with tape. The electrode was placed in distilled DMF and the solution was stirred for ca. 5 hours to dissolve the $(\text{C}_6\text{H}_5)(\text{CH}_3)_3\text{NPF}_6$ and increase porosity. 0.1495g of mix were used. The cathode had a thickness of 0.68mm.	$(\text{C}_6\text{H}_5)(\text{CH}_3)_3\text{NPF}_6\text{-DMF}$	Li
6. $\text{CuF}_2$	The composition was identical to that given for No. 5.	Ag expanded metal	The method of preparation was the same as that given for No. 5 except that the DMF solution was stirred for ca. 18 hours. 0.0819g of mix were used. The cathode had a thickness of 0.44mm.	$(\text{C}_6\text{H}_5)(\text{CH}_3)_3\text{NPF}_6\text{-DMF}$	Li
7. $\text{CuF}_2$	78 wt. % $\text{CuF}_2$ , 11 wt. % acetylene black, 11 wt. % Solka-Floc.	Ag expanded metal	0.1299g of the mixture were pressed on a $1\text{cm}^2$ matrix at a pressure of 10,000 lb/cm <sup>2</sup> . Filter paper was used to separate the pellet from the die*. The cathode had a thickness of 1.04mm.	$\text{LiClO}_4\text{-PC}$	Li

\* Filter paper was used to prevent formation of an impermeable electrode layer. The filter paper was removed after pressing.

TABLE IV. ELECTROCHEMICAL HALF-CELL SCREENING OF PRESSED INORGANIC CATHODES (Continued)

## A. Physical Details (Continued)

Active Cathode Material	Composition of Cathode Mix	Matrix	Method of Preparation	Electrolyte (1 molal)	Counter Electrode
8. CuF <sub>2</sub>	78 wt. % CuF <sub>2</sub> , 11 wt. % acetylene black, 11 wt. % Solka-Floc.	Cu expanded metal	0.1810g of the mixture were pressed on a 1cm <sup>2</sup> matrix at a pressure of 10,000 lb/cm <sup>2</sup> . The cathode had a thickness of 1.00mm.	LiClO <sub>4</sub> -PC	Li
9. CuF <sub>2</sub>	78 wt. % CuF <sub>2</sub> , 11 wt. % acetylene black, 11 wt. % Solka-Floc.	Ag expanded metal	The Solka-Floc and acetylene black additives were mixed in propylene carbonate. The solvent was filtered off and the precipitate was mixed with CuF <sub>2</sub> . The mixture was pressed on a 1cm <sup>2</sup> matrix at a pressure of 10,000 lb/cm <sup>2</sup> . Filter paper was used to separate the pellet from the die*. The cathode had a thickness of 1.07mm.	LiClO <sub>4</sub> -PC	Li
10. CuF <sub>2</sub>	85 wt. % CuF <sub>2</sub> , 5 wt. % acetylene black, 10 wt. % Solka-Floc.	Ag expanded metal	0.0418g of the mix were pressed on a 1cm <sup>2</sup> matrix at a pressure of 10,000 lb/cm <sup>2</sup> . The cathode had a thickness of 0.45mm. Adhesion of the active material to the matrix was poor.	LiClO <sub>4</sub> -PC	Li
11. CuF <sub>2</sub>	95 wt. % CuF <sub>2</sub> , 5 wt. % Cu.	Ag expanded metal	0.2760g of the mix were pressed on a 1cm <sup>2</sup> matrix at a pressure of 10,000 lb/cm <sup>2</sup> . The cathode had a thickness of 0.95mm.	LiClO <sub>4</sub> -PC	Li

\* Filter paper was used to prevent formation of an impenetrable electrode face. The filter paper was removed after pressing.



TABLE IV. ELECTROCHEMICAL HALF-CELL SCREENING OF PRESSED INORGANIC CATHODES (Continued)

## A. Physical Details (Continued)

Active Cathode Material	Composition of Cathode Mix	Matrix	Method of Preparation	Electrolyte (1 molal)	Counter Electrode
12. $\text{CuF}_2$	25 wt. % $\text{CuF}_2$ , 5 wt. % Cu.	Ag expanded metal	0.2056g of the mix were pressed on a $1\text{cm}^2$ matrix at a pressure of 10,000 lb/cm <sup>2</sup> . Filter paper was used to separate the pellet from the die*. The cathode had a thickness of 0.98mm.	$\text{LiClO}_4\text{-PC}$	Li
13. $\text{CuF}_2 + \text{SbF}_3$	50 wt. % $\text{CuF}_2$ , 50 wt. % $\text{SbF}_3$ .	Ag expanded metal	0.8832g of the mix were pressed on a $1\text{cm}^2$ matrix at a pressure of 15,000 lb/cm <sup>2</sup> .	$\text{LiClO}_4\text{-PC}$	Li
14. $\text{CuF}_2 + \text{SbF}_3$	78 wt. % $\text{CuF}_2$ , 11 wt. % $\text{SbF}_3$ , 11 wt. % Solka-Floc.	Cu expanded metal	0.4239g of the mixture were pressed on a $1\text{cm}^2$ matrix at a pressure of 10,000 lb/cm <sup>2</sup> . The cathode had a thickness of 1.48mm.	$\text{LiClO}_4\text{-PC}$	Li
15. $\text{CuF}_2 + \text{SbF}_3$	70 wt. % $\text{CuF}_2$ , 10 wt. % $\text{SbF}_3$ , 10 wt. % acetylene black, 10 wt. % Solka-Floc.	Cu expanded metal	0.3178g of the mix were pressed on a $1\text{cm}^2$ matrix at a pressure of 10,000 lb/cm <sup>2</sup> .	$\text{LiClO}_4\text{-PC}$	Li
16. $\text{NiF}_2$	85 wt. % $\text{NiF}_2$ , 10 wt. % Ni, 5 wt. % Solka-Floc.	Ni expanded metal	0.4667g of the mix were pressed on a $1\text{cm}^2$ matrix at a pressure of 10,000 lb/cm <sup>2</sup> .	$\text{LiClO}_4\text{-PC}$	Li

\* Filter paper was used to prevent formation of an impenetrable electrode face. The filter paper was removed after pressing.

TABLE IV. ELECTROCHEMICAL HALF-CELL SCREENING OF PRESSED INORGANIC CATHODES (Continued)

## A. Physical Details (Continued)

Active Cathode Material	Composition of Cathode Mix	Matrix	Method of Preparation	Electrolyte (1 molal)	Counter Electrode
17. Cu <sub>2</sub> S	43 wt. % Ag <sub>2</sub> O, 32 wt. % Cu, 18 wt. % S, 2 wt. % Solka-Floc.	Ag expanded metal	0.4333g of the mix were pressed on a 1cm <sup>2</sup> matrix at a pressure of 10,000 lb/cm <sup>2</sup> . The electrode was ignited* in air until the Solka-Floc was converted to carbon. Loss on ignition was 0.1193g. The resulting cathode was approximately 1.5mm thick and was gray with red flecks.	LiClO <sub>4</sub> -PC	Li
18. Cu <sub>2</sub> S	49 wt. % Cu <sub>2</sub> S, 24 wt. % Ag <sub>2</sub> O, 16 wt. % Cu, 9 wt. % S, 1 wt. % C, 1 wt. % Solka-Floc.	Ag expanded metal	0.4407g of the mix were pressed on a 1cm <sup>2</sup> matrix at a pressure of 10,000 lb/cm <sup>2</sup> . The electrode was ignited* in air until the Solka-Floc was converted to carbon. Loss on ignition was 0.0276g. The resulting cathode was 1.41mm thick and was gray in color.	LiClO <sub>4</sub> -PC	Li
19. NiF <sub>2</sub>	50 wt. % Ni, 50 wt. % AgF <sub>2</sub> .	Ag expanded metal	0.4437g of the mix were pressed on a 1cm <sup>2</sup> matrix at a pressure of 10,000 lb/cm <sup>2</sup> . The electrode was ignited* in air. Loss on ignition was 0.0243g. The resulting cathode was 1.07mm thick and was white in color.	LiClO <sub>4</sub> -PC	Li

\* The exact composition of the electrode, in terms of active cathode materials, was not determined after ignition.

TABLE IV. ELECTROCHEMICAL HALF-CELL SCREENING OF PRESSED INORGANIC CATHODES (Continued)

## A. Physical Details (Continued)

Active Cathode Material	Composition of Cathode Mix	Matrix	Method of Preparation	Electrolyte (1 molal)	Counter Electrode
20. NiO	75 wt. % Ni, 22 wt. % AgO, 3 wt. % Solka-Floc.	Ni expanded metal	0.9496g of the mix were pressed on a 1cm <sup>2</sup> matrix at a pressure of 10,000 lb/cm <sup>2</sup> . The electrode was ignited* in air until the Solka-Floc was converted to carbon. Loss on ignition was 0.0471g. The resulting cathode was 1.86mm thick and was gray in color.	LiClO <sub>4</sub> -PC	Li
21. NiO	50 wt. % Ni, 45 wt. % AgO, 5 wt. % Solka-Floc.	Ag expanded metal	0.5157g of the mix were pressed on a 1cm <sup>2</sup> matrix at a pressure of 10,000 lb/cm <sup>2</sup> . The electrode was ignited* in air until the Solka-Floc was converted to carbon. Loss on ignition was 0.1447g. The resulting cathode was 1.07mm thick and was gray in color.	LiClO <sub>4</sub> -PC	Li
22. AgO	95 wt. % AgO, 5 wt. % Solka-Floc.	Ag expanded metal	A small amount of the mix was pressed on a 1cm <sup>2</sup> matrix at a pressure of 10,000 lb/cm <sup>2</sup> . The electrode was ignited* in air until the Solka-Floc was converted to carbon. The resulting cathode weighed 0.5398g (not including the matrix), was 2.35mm thick and was white in color.	LiClO <sub>4</sub> -PC	Li

\* The exact composition of the electrode, in terms of active cathode materials, was not determined after ignition.

TABLE IV. ELECTROCHEMICAL HALF-CELL SCREENING OF PRESSED INORGANIC CATHODES (Continued)

## A. Physical Details (Continued)

Active Cathode Material	Composition of Cathode Mix	Matrix	Method of Preparation	Electrolyte (1 molar)	Counter Electrode
23. AgO + SbF <sub>3</sub>	85.5 wt. % AgO, 10 wt. % SbF <sub>3</sub> , 4.5 wt. % Solka-Floc.	Ag expanded metal	0.4641g of the mixture were pressed on a 1cm <sup>2</sup> matrix at a pressure of 10,000 lb/cm <sup>2</sup> . The cathode had a thickness of 1.35mm.	LiClO <sub>4</sub> -PC	Li
24. AgO + CuF <sub>2</sub>	50 wt. % CuF <sub>2</sub> , 45 wt. % AgO, 5 wt. % Solka-Floc.	Ag expanded metal	0.4739g of the mix were pressed on a 1cm <sup>2</sup> matrix at a pressure of 10,000 lb/cm <sup>2</sup> . Filter paper was used to separate the pellet from the die*. The cathode had a thickness of 1.43mm.	LiClO <sub>4</sub> -PC	Li
25. CuF <sub>2</sub>	50 wt. % CuF <sub>2</sub> , 45 wt. % AgO, 5 wt. % Solka-Floc.	Ag expanded metal	0.5853g of the mix were pressed on a 1cm <sup>2</sup> matrix at a pressure of 10,000 lb/cm <sup>2</sup> . The electrode was ignited* in air until the Solka-Floc was converted to carbon. Loss on ignition was 0.0989g. The resulting cathode was 1.75mm thick and was dark gray in color.	LiClO <sub>4</sub> -PC	Li

\* Filter paper was used to prevent formation of an impenetrable electrode face. The filter paper was removed after pressing.

\*\* The exact composition of the electrode, in terms of active cathode materials, was not determined after ignition.

TABLE IV. ELECTROCHEMICAL HALF-CELL SCREENING OF PRESSED INORGANIC CATHODES (Continued)

## A. Physical Details (Continued)

Active Cathode Material	Composition of Cathode Mix	Matrix	Method of Preparation	Electrolyte (1 molal)	Counter Electrode
26. CuF <sub>2</sub>	48 wt. % Ag <sub>2</sub> O, 33 wt. % CuF <sub>2</sub> , 5 wt. % acetylene black, 2 wt. % Solka-Floc.	Ag expanded metal	A small amount of the mix was pressed on a 1cm <sup>2</sup> matrix at a pressure of 15,000 lb/cm <sup>2</sup> . The electrode was ignited* in air until the Solka-Floc was converted to carbon. The resulting cathode weighed 0.3999g (not including the matrix), was approximately 2mm thick and was gray in color.	LiClO <sub>4</sub> -PC	Li
27. CoF <sub>3</sub>	50 wt. % CoF <sub>3</sub> , 45 wt. % Ag <sub>2</sub> O, 5 wt. % Solka-Floc.	Ag expanded metal	0.3625g of the mix were pressed on a 1cm <sup>2</sup> matrix at a pressure of 10,000 lb/cm <sup>2</sup> . The pellet was ignited* in air until the Solka-Floc was converted to carbon. Loss on ignition was 0.0777g. The resulting cathode was 1.54mm thick and was gray-white in color.	LiClO <sub>4</sub> -PC	Li
28. TiF <sub>3</sub>	85 wt. % TiF <sub>3</sub> , 15 wt. % Solka-Floc.	Ag expanded metal	0.2136g of the mix were pressed on a 1cm <sup>2</sup> matrix at a pressure of 10,000 lb/cm <sup>2</sup> . The resulting cathode was 1.25mm thick.	LiClO <sub>4</sub> -PC	Li

\* The exact composition of the electrode, in terms of active cathode materials, was not determined after ignition.

TABLE IV. ELECTROCHEMICAL HALF-CELL SCREENING OF PRESSED INORGANIC CATHODES

## B. Electrochemical Details for Cathodes Evaluated in Five Minute Discharges at Various Current Densities

Active Cathode Material	Electrolyte (1 molar)	Counter Electrode	Time of Measurement	Voltage of Cathode vs. Ag/AgCl Reference Electrode at Various Current Densities* (ma/cm <sup>2</sup> )								
				0	0.1	1	5	10	15	20	25	50
1. CuF <sub>2</sub>	(C <sub>6</sub> H <sub>5</sub> )(CH <sub>3</sub> ) <sub>3</sub> NPF <sub>6</sub> -DMF	Li	Initial Final	+0.26 -0.03	+0.23 +0.16	+0.07 -0.03	-0.15 -0.57	-0.50 -1.04	** **	** **	-0.90 -2.00	** **
Note: The original dark green electrolyte was yellow at the end of the discharges.												
2. CuF <sub>2</sub>	(C <sub>6</sub> H <sub>5</sub> )(CH <sub>3</sub> ) <sub>3</sub> NPF <sub>6</sub> -DMF	Li	Initial Final	+0.22 **	+0.19 +0.14	+0.02 -0.09	-0.22 -0.51	-0.80 -1.36	** **	** **	** -2.00 (7 min.)	-2.23 -2.22
3. CuF <sub>2</sub>	LiClO <sub>4</sub> -PC	Li	Initial Final	+0.64 **	+0.60 +0.48	+0.30 +0.24	-0.04 -3.20	** ** (16 min.)	** **	** **	** **	** **
4. CuF <sub>2</sub>	(C <sub>6</sub> H <sub>5</sub> )(CH <sub>3</sub> ) <sub>3</sub> NPF <sub>6</sub> -DMF	Li	Initial Final	+0.39 -0.08	+0.34 +0.22	+0.12 +0.04	-0.15 -1.6	-0.8 -1.9 (1 hr.) (20 min.)	** **	** **	-2.0 -2.2 (33 min.)	** **
5. CuF <sub>2</sub>	(C <sub>6</sub> H <sub>5</sub> )(CH <sub>3</sub> ) <sub>3</sub> NPF <sub>6</sub> -DMF	Li	Initial Final	+0.01 -0.59	+0.01 +0.01	-0.1 -0.18	-0.16 -0.77	-0.5 -1.3	** **	** **	-1.0 -1.85 (10 min.)	** **
Note: The electrolyte changed from dark green to yellow.												

\* Duration of discharge at each current density - 5 minutes (unless noted otherwise).  
 \*\* Not run.

TABLE IV. ELECTROCHEMICAL HALF-CELL SCREENING OF PRESSED INORGANIC CATHODES (Continued)

B. Electrochemical Details for Cathodes Evaluated in Five Minute Discharges at Various Current Densities (continued)

Active Cathode Material	Electrolyte (1 molar)	Counter Electrode	Time of Measurement	Voltage of Cathode vs. Ag/AgCl Reference Electrode at Various Current Densities* (ma/cm <sup>2</sup> )									
				0	0.1	1	5	10	15	20	25	50	
6. CuF <sub>2</sub>	(C <sub>6</sub> H <sub>5</sub> )(CH <sub>3</sub> ) <sub>3</sub> NPF <sub>6</sub> -DMF	Li	Initial Final	+0.21 -0.6	+0.19 +0.12	-0.02 -0.06	-0.20 -1.24	-1.0 -1.72	** **	** **	-2.0 -2.6	** **	
Note: The cathode and counter electrode began gassing during the 25 ma/cm <sup>2</sup> discharge.													
7. CuF <sub>2</sub>	LiClO <sub>4</sub> -PC	Li	Initial Final	+0.38 +0.02	+0.37 +0.35	+0.32 +0.13	+0.03 -0.04	-0.15 -0.25	-0.37 -0.49	-0.51 -0.73	-0.64 -0.96	** **	
9. CuF <sub>2</sub>	LiClO <sub>4</sub> -PC	Li	Initial Final	+0.55 -0.03	+0.55 +0.41	+0.36 +0.28	+0.05 -0.10	-0.37 -0.63	-0.75 -1.22	** **	** **	** **	
10. CuF <sub>2</sub>	LiClO <sub>4</sub> -PC	Li	Initial Final	+0.52 -0.01	+0.50 +0.46	+0.40 +0.23	+0.10 +0.01	-0.18 -0.41	-0.33 -0.72	-0.72 -1.09	** **	** **	
11. CuF <sub>2</sub>	LiClO <sub>4</sub> -PC	Li	Initial Final	+0.49 +0.33	+0.45 +0.43	+0.35 +0.26	-0.10 -0.56	-0.40 -1.19	** **	** **	** **	** **	
12. CuF <sub>2</sub>	LiClO <sub>4</sub> -PC	Li	Initial Final	+0.48 +0.25	+0.44 +0.42	+0.35 +0.29	+0.03 -0.63	-0.18 -1.21	** **	** **	** **	** **	

\* Duration of discharge at each current density - 5 minutes (unless noted otherwise).

\*\* Not run.

TABLE IV. ELECTROCHEMICAL HALF-CELL SCREENING OF PRESSED INORGANIC CATHODES (Continued)

## B. Electrochemical Details for Cathodes Evaluated in Five Minute Discharges at Various Current Densities (Continued)

Voltage of Cathode vs. Ag/AgCl Reference Electrode at Various												
Active Cathode Material	Electrolyte (1 molal)	Counter Electrode	Time of Measurement	Current Densities* (ma/cm <sup>2</sup> )								
				0	0.1	1	5	10	15	20	30	
13. CuF <sub>2</sub> + SbF <sub>3</sub>	LiClO <sub>4</sub> -PC	Li	Initial	+0.66	+0.59	+0.25	-0.67	**	**	**	**	**
			Final	+0.42	+0.46	+0.20	-1.05	**	**	**	**	**
15. CuF <sub>2</sub> + SbF <sub>3</sub>	LiClO <sub>4</sub> -PC	Li	Initial	**	**	**	0.00	-0.38	-0.92	-0.70	-1.10	
			Final	**	**	**	-0.23	-0.41	-1.00	-1.40	-1.53	
16. NiF <sub>2</sub>	LiClO <sub>4</sub> -PC	Li	Initial	+0.06	-0.76	-0.94	**	**	**	**	**	
			Final	-0.34	-0.59	-1.52	**	**	**	**	**	
				(3 min.)								
17. Cu <sub>2</sub> S	LiClO <sub>4</sub> -PC	Li	Initial	+0.22	+0.19	-0.15	-0.80	**	**	**	**	
			Final	-0.27	0.00	-0.53	-1.04	**	**	**	**	
				(1 min.)								
18. Cu <sub>2</sub> S	LiClO <sub>4</sub> -PC	Li	Initial	+0.55	+0.54	+0.49	+0.24	-0.20	**	**	**	
			Final	+0.10	+0.51	+0.28	-0.46	-1.08	**	**	**	
				(3 min.)								
19. NiF <sub>2</sub>	LiClO <sub>4</sub> -PC	Li	Initial	+0.61	+0.59	-0.20	**	**	**	**	**	
			Final	-0.25	+0.02	-1.18	**	**	**	**	**	
				(1 min.)								
20. NiO	LiClO <sub>4</sub> -PC	Li	Initial	+0.27	+0.27	+0.16	**	**	**	**	**	
			Final	-0.07	+0.14	-1.12	**	**	**	**	**	
				(3 min.)								

\* Duration of discharge at each current density - 5 minutes (unless noted otherwise).

\*\* Not run.



TABLE IV. ELECTROCHEMICAL HALF-CELL SCREENING OF PRESSED INORGANIC CATHODES (Continued)

B. Electrochemical Details for Cathodes Evaluated in Five Minute Discharges at Various Current Densities (Continued)

Active Cathode Material	Electrolyte (1 molal)	Counter Electrode	Time of Measurement	Voltage of Cathode vs. Ag/AgCl Reference Electrode at Various Current Densities* (ma/cm <sup>2</sup> )				
				0	0.1	1	5	10
21. NiO	LiClO <sub>4</sub> -PC	Li	Initial Final	-0.01 -0.40	-0.04 -0.92	-0.70 -1.24 (1 min.)	** **	** **
22. AgO	LiClO <sub>4</sub> -PC	Li	Initial Final	+0.16 -0.53	+0.10 -0.37	-0.50 -1.40 (1 min.)	** **	** **
24. AgO + CuF <sub>2</sub>	LiClO <sub>4</sub> -PC	Li	Initial Final	+0.36 +0.40	+0.34 +0.35	+0.26 +0.24 (3 min.)	-0.17 -1.78 (3 min.)	** **
25. CuF <sub>2</sub>	LiClO <sub>4</sub> -PC	Li	Initial Final	+0.21 -0.07	+0.21 -0.18	+0.13 -0.10	-0.19 -0.73 (3 min.)	-0.70 -1.02 (3 min.)
26. CuF <sub>2</sub>	LiClO <sub>4</sub> -PC	Li	Initial Final	-0.05 -0.55	-0.20 -0.85	-1.00 -1.20 (1 min.)	** **	** **
27. CoF <sub>3</sub>	LiClO <sub>4</sub> -PC	Li	Initial Final	+0.69 -0.45	+0.69 +0.67	+0.64 -0.70 (1 min.)	-0.70 -1.15 (1 min.)	** **
28. TiF <sub>3</sub>	LiClO <sub>4</sub> -PC	Li	Initial Final	+0.21 -0.11	0.00 -0.08	-0.29 -0.75 (1 min.)	-1.20 -1.57 (1 min.)	** **

\* Duration of discharge at each current density - 5 minutes (unless noted otherwise).

\*\* Not run.

TABLE IV. ELECTROCHEMICAL HALF-CELL SCREENING OF PRESSED INORGANIC CATHODES (Continued)

C. Electrochemical Details for Cathodes Evaluated From Linearly Varying Potential Scans

Active Cathode Material	Electrolyte (1 molal)	Counter Electrode	Voltage of Cathode vs. Ag/AgCl Reference Electrode at Various Current Densities* (ma/cm <sup>2</sup> )											
			0	0.1	1	5	10	15	20	25	40	50	70	80
8. CuF <sub>2</sub>	LiClO <sub>4</sub> -PC	Li	+0.48	+0.30	+0.25	+0.20	0.00	**	-0.40	**	-1.0	**	**	**
14. CuF <sub>2</sub> + SbF <sub>3</sub>	LiClO <sub>4</sub> -PC	Li	+0.35	+0.25	+0.20	+0.15	+0.10	**	0.0	**	-0.25	-0.5	-1.0	-1.20
23. AgO + SbF <sub>3</sub>	LiClO <sub>4</sub> -PC	Li	+0.84	+0.5	+0.4	0.0	-0.5	-1.25	**	**	**	**	**	**

\* These voltage readings were recorded from linearly varying potential scans. Five minute discharges at each current density were not run.

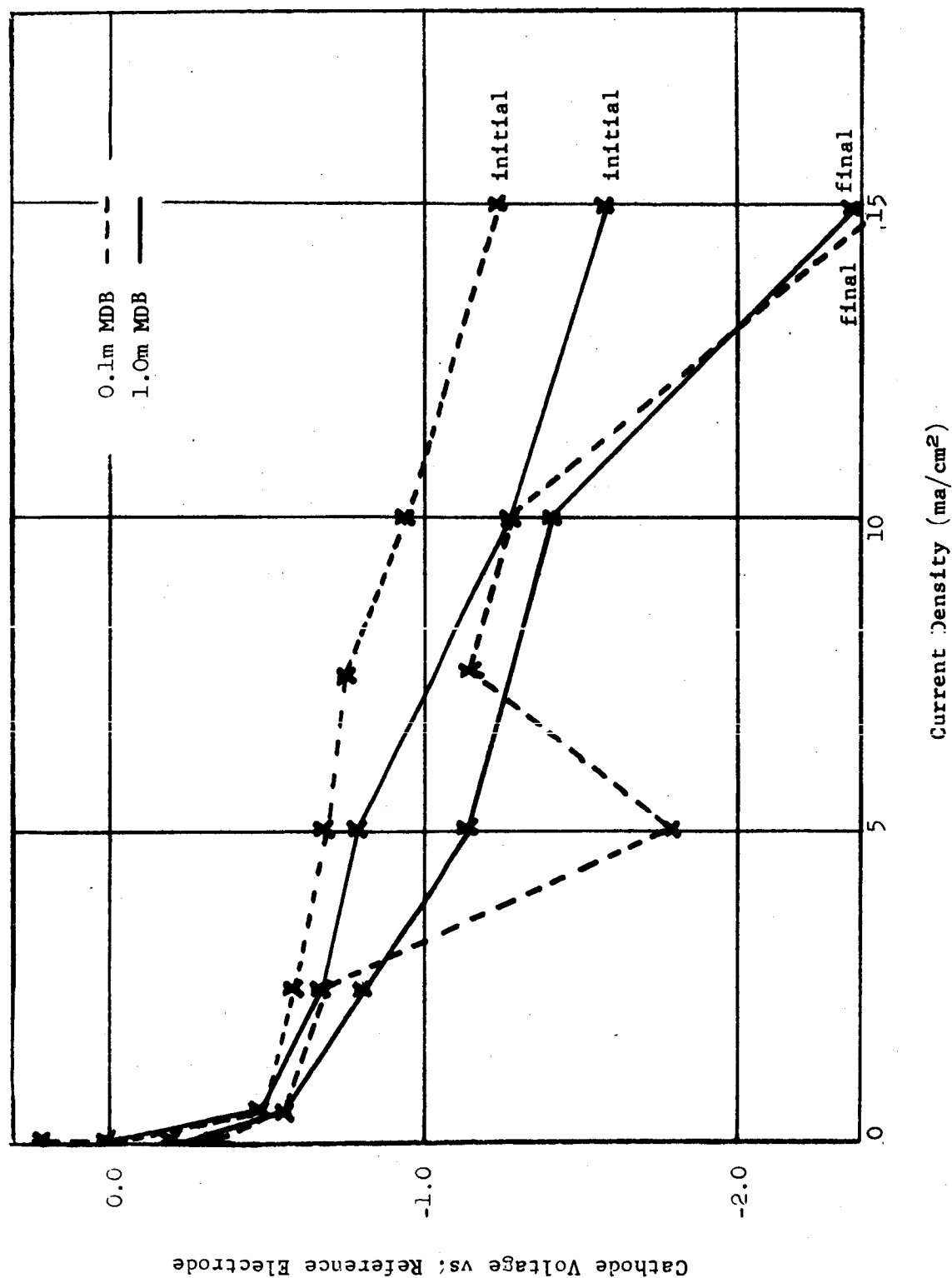
\*\* Not run.

FIGURE 1. ELECTROCHEMICAL HALF-CELL SCREENING OF  
DISSOLVED ACTIVE ORGANIC CATHODE MATERIALS

	Active Cathode Material	Concentration (Molal)	Electrodes		Electrolyte (1 molal)	Page
			Working	Counter		
a.	M-Dinitrobenzene (MDB)	0.1,1.0	Carbon	Carbon	LiPF <sub>6</sub> - Dimethyl- formamide (DMF)	IV-21
b.	Trichloroisocyanuric Acid (ACL-85)	0.1,1.0	Carbon	Li	AlCl <sub>3</sub> -Ace- tonitrile	IV-22
c.	ACL-85	0.1,1.0	Carbon	Li	LiPF <sub>6</sub> -DMF	IV-23
d.	ACL-85	0.1,1.0	Carbon	Carbon	LiPF <sub>6</sub> -DMF	IV-24
e.	ACL-85	1.0	Carbon	Carbon	LiPF <sub>6</sub> -DMF	IV-25
f.	Trichloromelamine (TCM) Gel	1.0	Carbon Cu Screen Ag expanded metal	Li	LiPF <sub>6</sub> -DMF	IV-26
g.	TCM	0.1,1.0	Carbon	Carbon	LiPF <sub>6</sub> -DMF	IV-27
h.	TCM	0.1	Carbon	Carbon	LiPF <sub>6</sub> -DMF and LiPF <sub>6</sub> - N-Nitro- sodimethyl- amine	IV-28
i.	Hexachloromelamine	0.1,1.0	Carbon	Li	LiPF <sub>6</sub> -DMF	IV-29
j.	HCM	0.1,1.0	Carbon	Carbon	LiPF <sub>6</sub> -DMF	IV-30
k.	ACL-85, HCM	0.1	Carbon	Li	LiPF <sub>6</sub> -DMF	IV-31
l.	ACL-85, TCM, HCM	1.0	Carbon	Li	LiPF <sub>6</sub> -DMF	IV-31
m.	ACL-85, TCM, HCM	0.1	Carbon	Carbon	LiPF <sub>6</sub> -DMF	IV-32
n.	ACL-85, TCM, HCM	1.0	Carbon	Carbon	LiPF <sub>6</sub> -DMF	IV-32

FIGURE 1. ELECTROCHEMICAL HALF-CELL SCREENING OF DISSOLVED ACTIVE ORGANIC CATHODE MATERIALS\*.

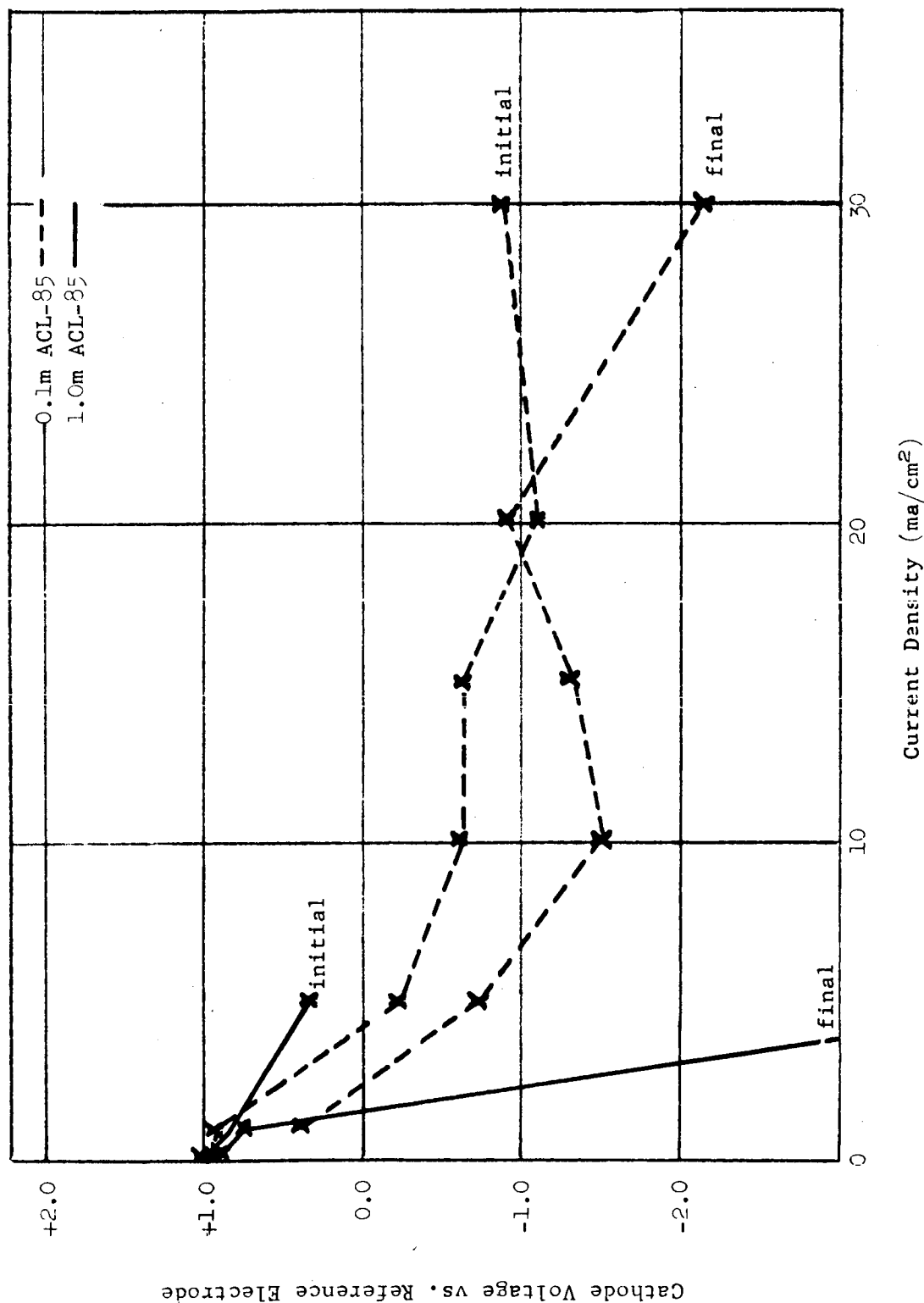
FIGURE 1a. M-DINITROBENZENE. WORKING AND COUNTER ELECTRODES - HP-10 SPEER CARBON (2cm<sup>2</sup>). REFERENCE ELECTRODES - Ag/AgCl. ELECTROLYTES - LiPF<sub>6</sub>-DIMETHYL-FORMAMIDE (1 MOLAL).



\* Voltages are initial and final values for a 5 minute test at the indicated (X) current densities.

FIGURE 1. ELECTROCHEMICAL HALF-CELL SCREENING OF DISSOLVED ACTIVE ORGANIC CATHODE MATERIALS\*. (Continued)

FIGURE 1b. TRICHLOROISOCYANURIC ACID (ACL-85). WORKING ELECTRODES - HP-10 SPEER CARBON (1cm<sup>2</sup>). COUNTER ELECTRODES - Li\*\*. REFERENCE ELECTRODES - Ag/AgCl. ELECTROLYTES - AlCl<sub>3</sub> - ACETONITRILE (1 MOLAL).

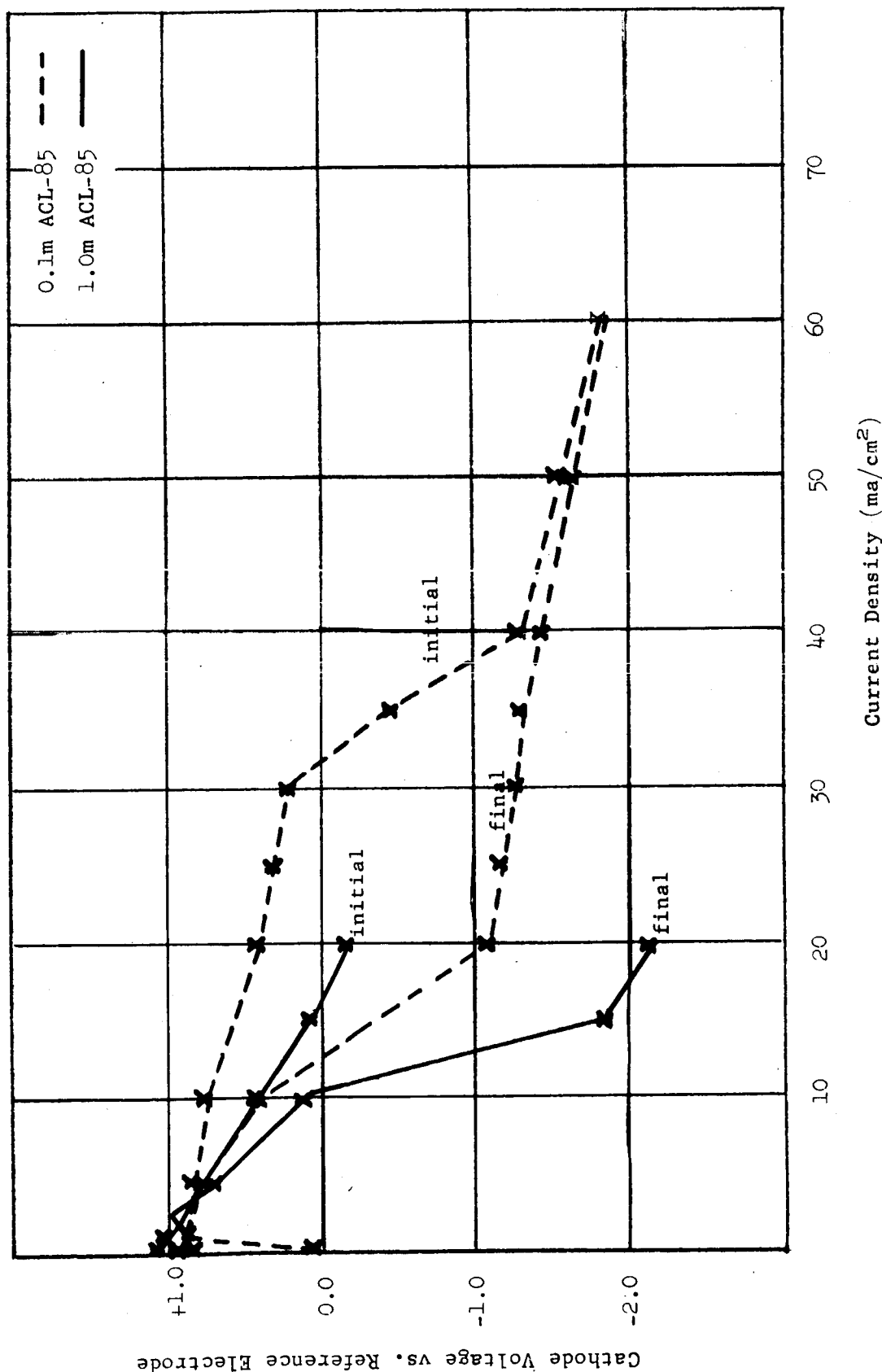


\* Voltages are initial and final values for a 5 minute test at the indicated (X) current densities.

\*\* Li appeared to be stable in the 1m ACL-85 system but caused some discoloration of the electrolyte in the 0.1m ACL-85 system.

FIGURE 1. ELECTROCHEMICAL HALF-CELL SCREENING OF DISSOLVED ACTIVE ORGANIC CATHODE MATERIALS\* (Continued)

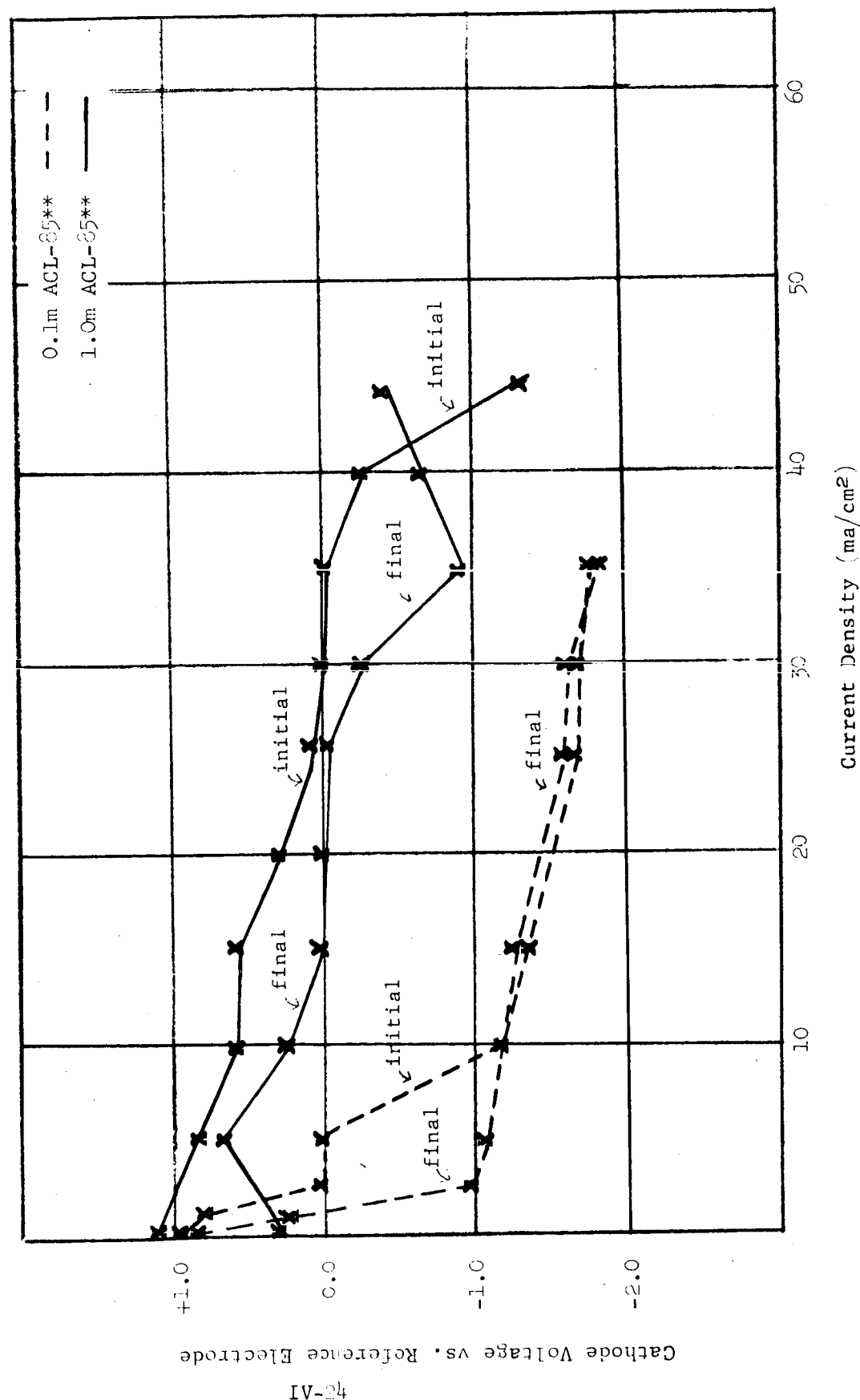
FIGURE 1c. TRICHLOROISOCYANURIC ACID (ACL-85). WORKING ELECTRODES - HP-10 SPEER CARBON ( $1\text{cm}^2$ ). COUNTER ELECTRODES - Li\*\*. REFERENCE ELECTRODES - Ag/AgCl. ELECTROLYTES -  $\text{LiPF}_6$ -DIMETHYLFORMAMIDE (1 MOLAL).



\* Voltages are initial and final values for a 5 minute test at the indicated (X) current densities.  
 \*\* Li appeared to be stable in the 1m ACL-85 system but caused some discoloration of the electrolyte in the 0.1m ACL-85 system.

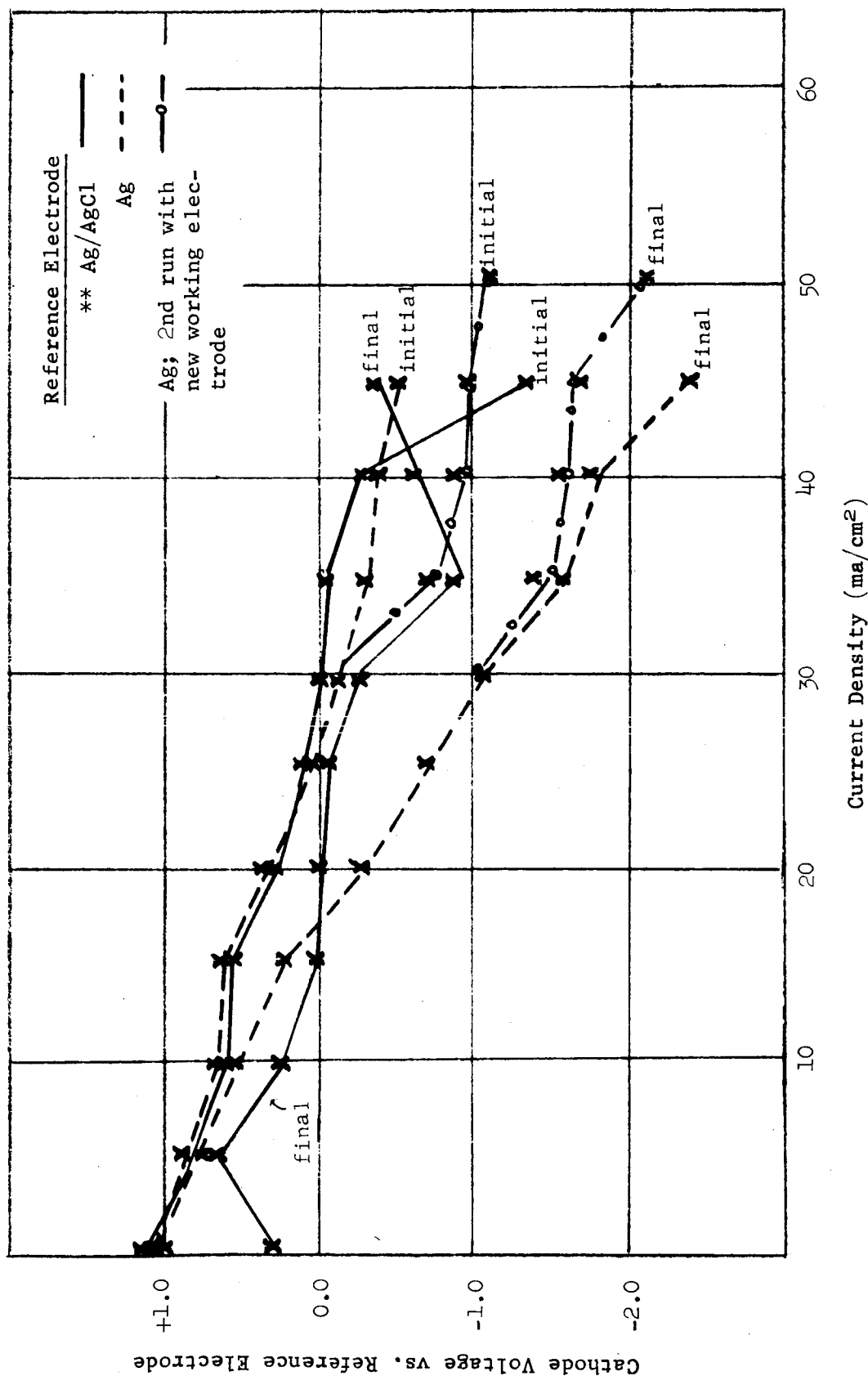
FIGURE 1. ELECTROCHEMICAL HALF-CELL SCREENING OF DISSOLVED ACTIVE ORGANIC MATERIALS\* (Continued)

FIGURE 1d. TRICHLOROISOCYANURIC ACID (ACL-85), WORKING AND COUNTER ELECTRODES - HP-10 SPEER CARBON (2 cm<sup>2</sup>). REFERENCE ELECTRODES - Ag/AgCl. ELECTROLYTES - LiPF<sub>6</sub>-DIMETHYLFORMAMIDE (1 MOLAL).



\* Voltages are initial and final values for a 5 minute test at the indicated (X) current densities.  
 \*\* Working and reference electrodes were periodically replaced because of film formation on the working electrode surface and deterioration of the reference electrode.

FIGURE 1e. TRICHLOROISOCYANURIC ACID (ACL-85). WORKING AND COUNTER ELECTRODES - HP-10 SPEER CARBON ( $2\text{cm}^2$ ). ELECTROLYTES -  $\text{LiPF}_6$ -DIMETHYLFORMAMIDE (1 MOLAL).

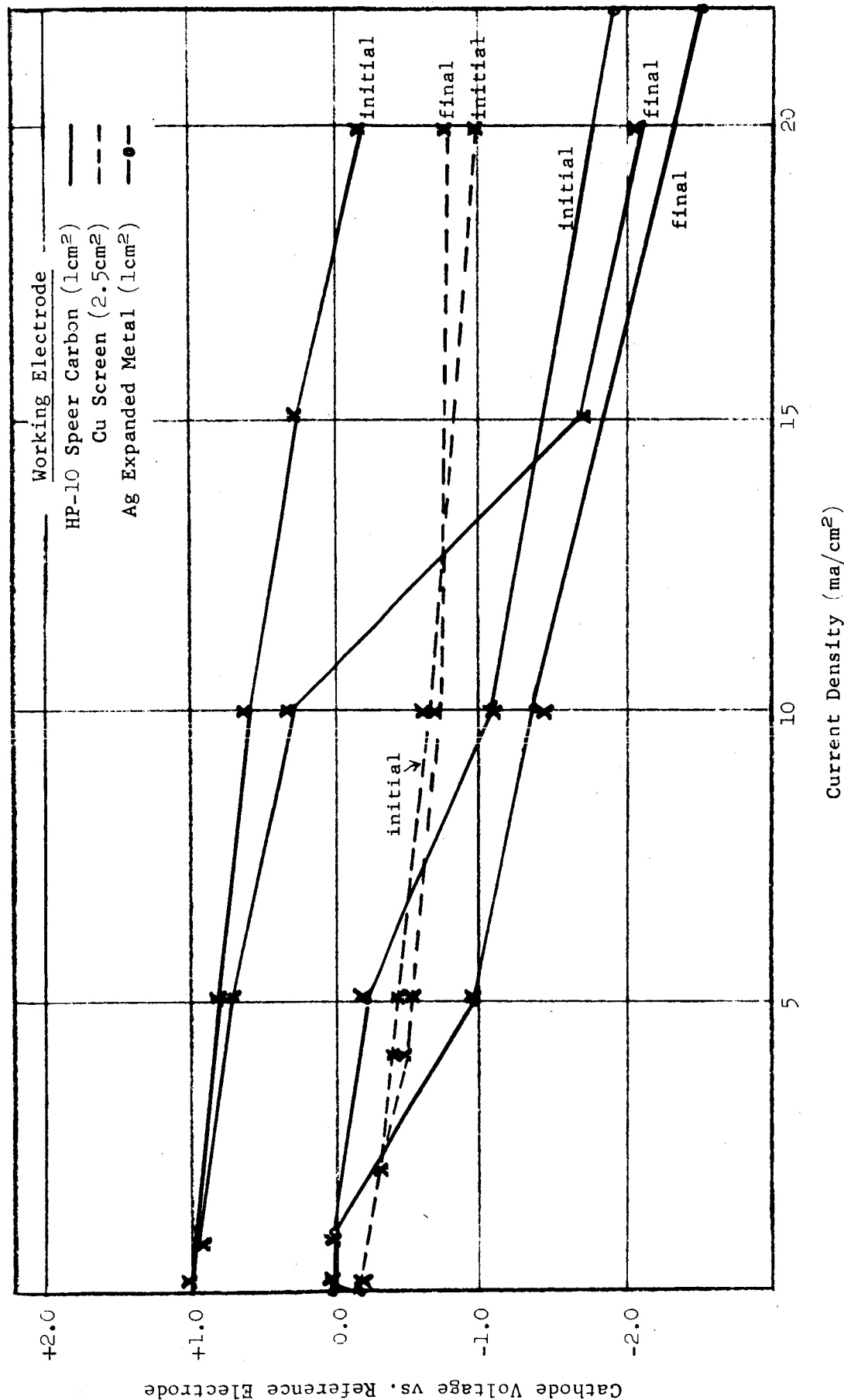


\* Voltages are initial and final values for a 5 minute test at the indicated (X) current densities.  
 \*\* Working and reference electrodes were periodically replaced because of film formation on the working electrode surface and deterioration of the reference electrode.



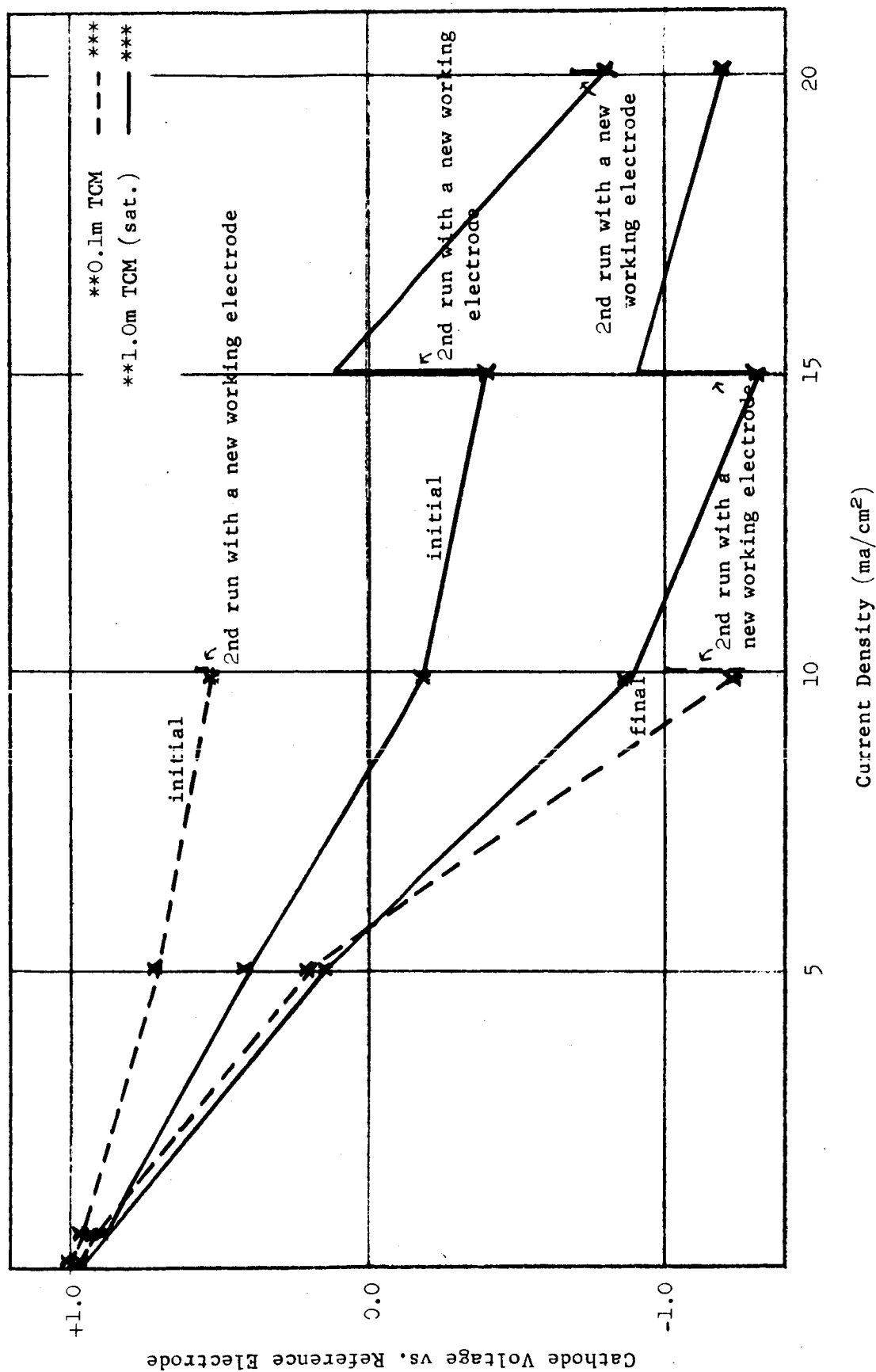
FIGURE 1. ELECTROCHEMICAL HALF-CELL SCREENING OF DISSOLVED ACTIVE ORGANIC CATHODE MATERIALS\* (Continued)

FIGURE 1f. TRICHLOROMELAMINE GEL\*\* (1 MOLAL, SATURATED). COUNTER ELECTRODES - Li\*\*\*. REFERENCE ELECTRODES - Ag/AgCl. ELECTROLYTES - LiPF<sub>6</sub>-DIMETHYLFORMAMIDE (1 MOLAL).



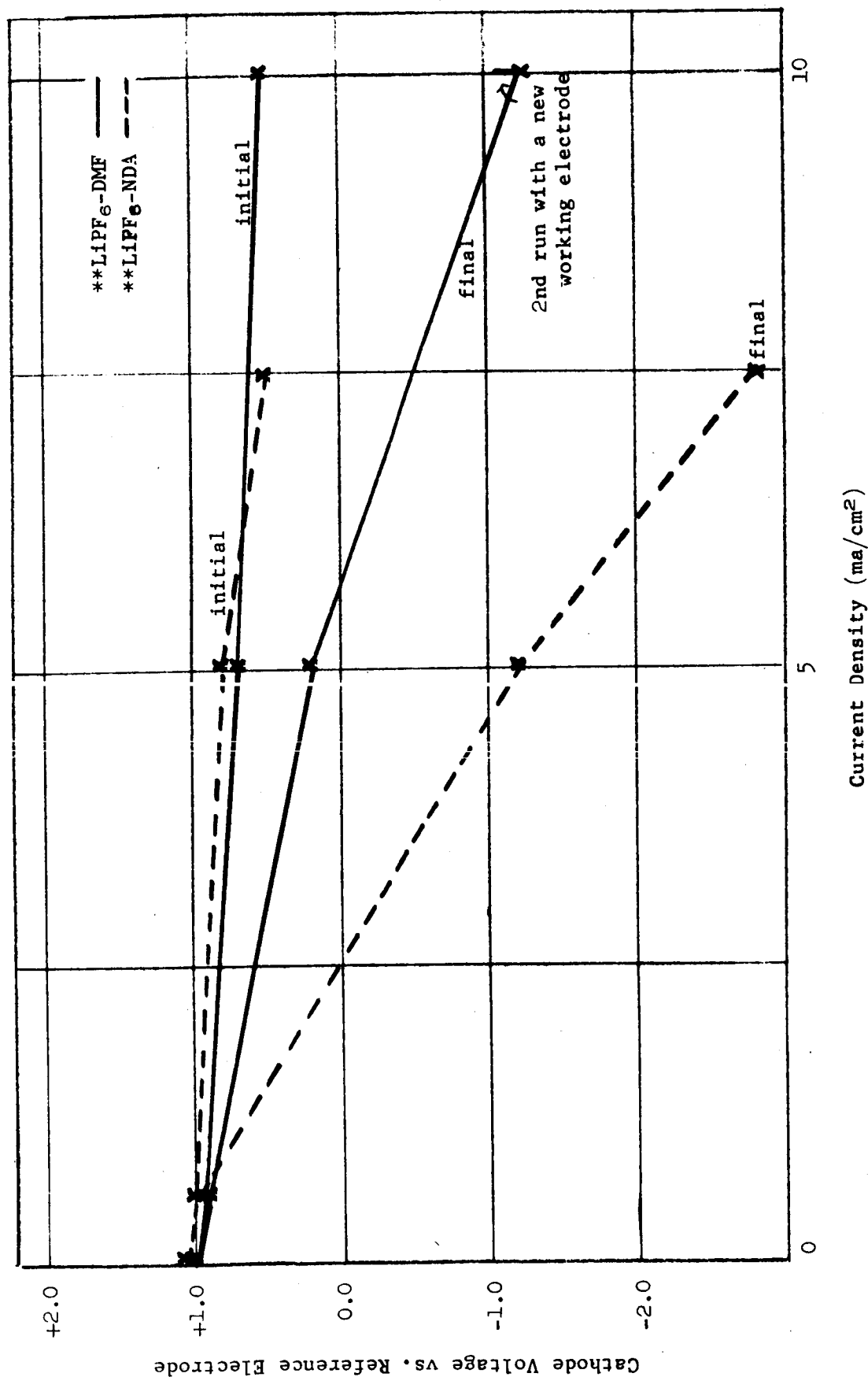
\* Voltages are initial and final values for a 5 minute test at the indicated (X) current densities.  
 \*\* When 1m LiPF<sub>6</sub>-DMF was made 1m in TCM within several days the entire solution reacted to form a gelatinous substance.  
 \*\*\* Li appeared to be stable in these systems for the duration of the test.

FIGURE 1g. TRICHLOROMELAMINE. WORKING AND COUNTER ELECTRODES - HP-10 SPEER CARBON ( $2\text{cm}^2$ ).  
REFERENCE ELECTRODES - Ag/AgCl. ELECTROLYTES -  $\text{LiPF}_6$ -DIMETHYLFORMAMIDE (1 MOLAL).



\* Voltages are initial and final values for a 5 minute test at the indicated (X) current densities.  
 \*\* The solution was not gelled.  
 \*\*\* Working and reference electrodes were periodically replaced because of film formation on the working electrode surface and deterioration of the reference electrode.

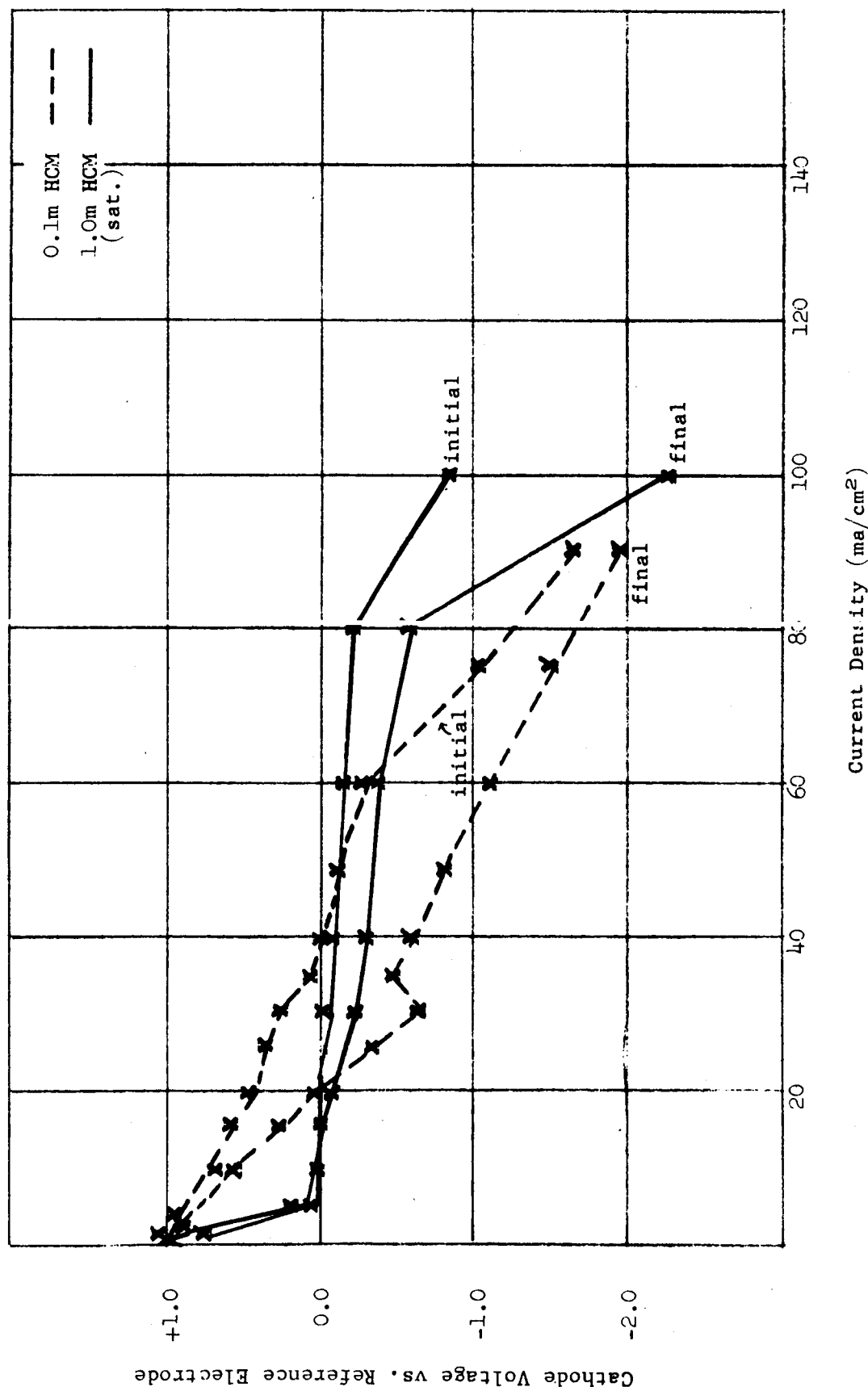
FIGURE 1h. TRICHLOROMELAMINE (0.1 MOLAL). WORKING AND COUNTER ELECTRODES - HP-10 SPEER CARBON (2cm<sup>2</sup>). REFERENCE ELECTRODES - Ag/AgCl IN DIMETHYLFORMAMIDE; Ag IN N-NITROSODIMETHYL-AMINE. ELECTROLYTES - LiPF<sub>6</sub> IN DIMETHYLFORMAMIDE AND N-NITROSODIMETHYLAMINE (1 MOLAL).



\* Voltages are initial and final values for a 5 minute test at the indicated (X) current densities.  
 \*\* The solution was not gelled.

FIGURE 1. ELECTROCHEMICAL HALF-CELL SCREENING OF DISSOLVED ACTIVE ORGANIC CATHODE MATERIALS\* (Continued)

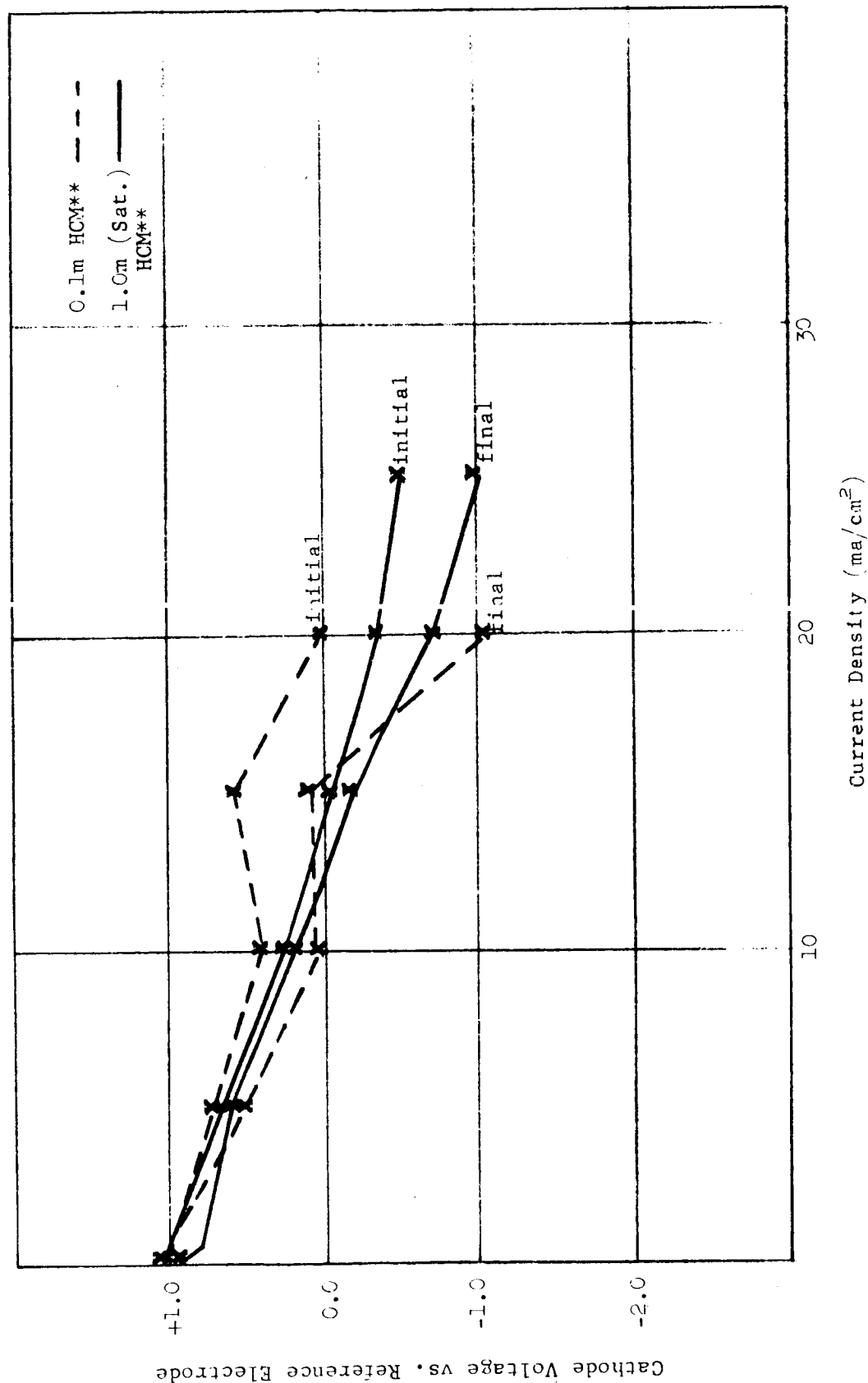
FIGURE 11. HEXACHLOROMELAMINE. WORKING ELECTRODES - HP-10 SPEER CARBON ( $1\text{cm}^2$ ). COUNTER ELECTRODES - Li\*\*. REFERENCE ELECTRODES - Ag/AgCl. ELECTROLYTES -  $\text{LiPF}_6$ -DIMETHYLFORMAMIDE (1 MOLAL).



\* Voltages are initial and final values for a 5 minute test at the indicated (X) current densities.  
 \*\* Li became covered with a white solid during the discharge of the 1m HCM system. Li appeared to be stable in the 0.1m HCM system.

FIGURE 1. ELECTROCHEMICAL HALF-CELL SCREENING OF DISSOLVED ACTIVE ORGANIC CATHODE MATERIALS\* (Continued)

FIGURE 1j. HEXACHLOROMELAMINE. WORKING AND COUNTER ELECTRODES - HP-10 SPEER CARBON ( $2\text{cm}^2$ ). REFERENCE ELECTRODES - Ag/AgCl. ELECTROLYTES -  $1\text{M}$  PF<sub>6</sub>-DIMETHYLFORMAMIDE ( $1\text{MOLAL}$ ).  
 0.1m HCM\*\*    - - -  
 1.0m (Sat.)    - - -  
 HCM\*\*    - - -

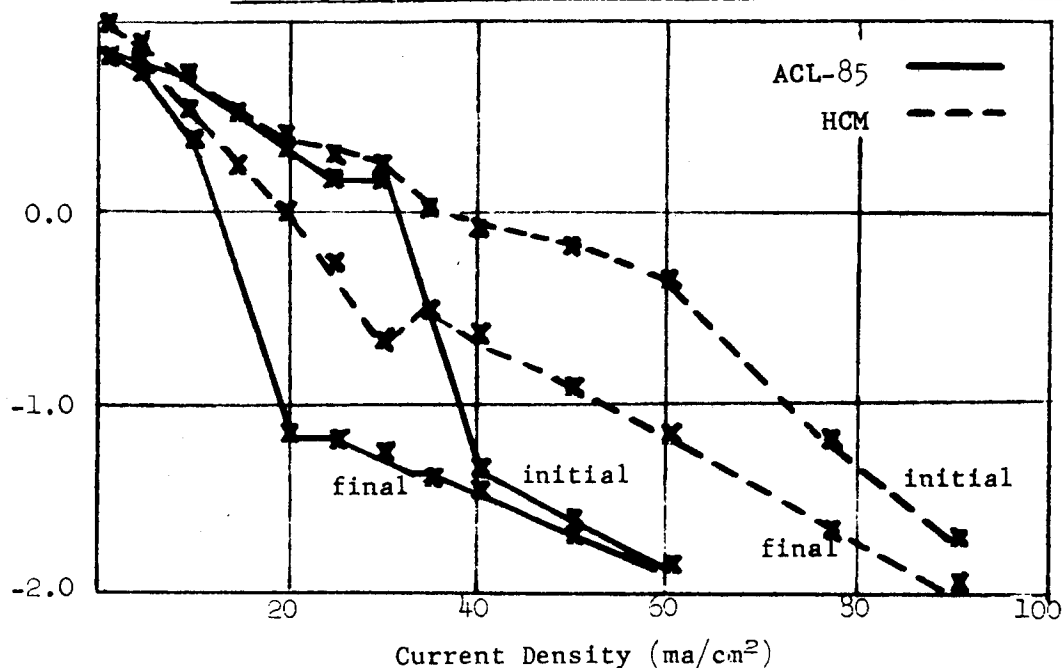


\* Voltages are initial and final values for a 5 minute test at the indicated (X) current densities.  
 \*\* Working and reference electrodes were periodically replaced because of film formation on the working electrode surface and deterioration of the reference electrode.

FIGURE 1. ELECTROCHEMICAL HALF-CELL SCREENING OF DISSOLVED ACTIVE ORGANIC CATHODE MATERIALS (Continued)

FIGURE 1k. A COMPARISON OF POSITIVE HALOGEN COMPOUNDS (0.1 MOLAL) IN  $\text{LiPF}_6$ -DIMETHYLFORMAMIDE (1 MOLAL). WORKING ELECTRODES - HP-10 SPEER CARBON ( $1\text{cm}^2$ ). COUNTER ELECTRODES -  $\text{Li}^*$ . REFERENCE ELECTRODES -  $\text{Ag}/\text{AgCl}$ .

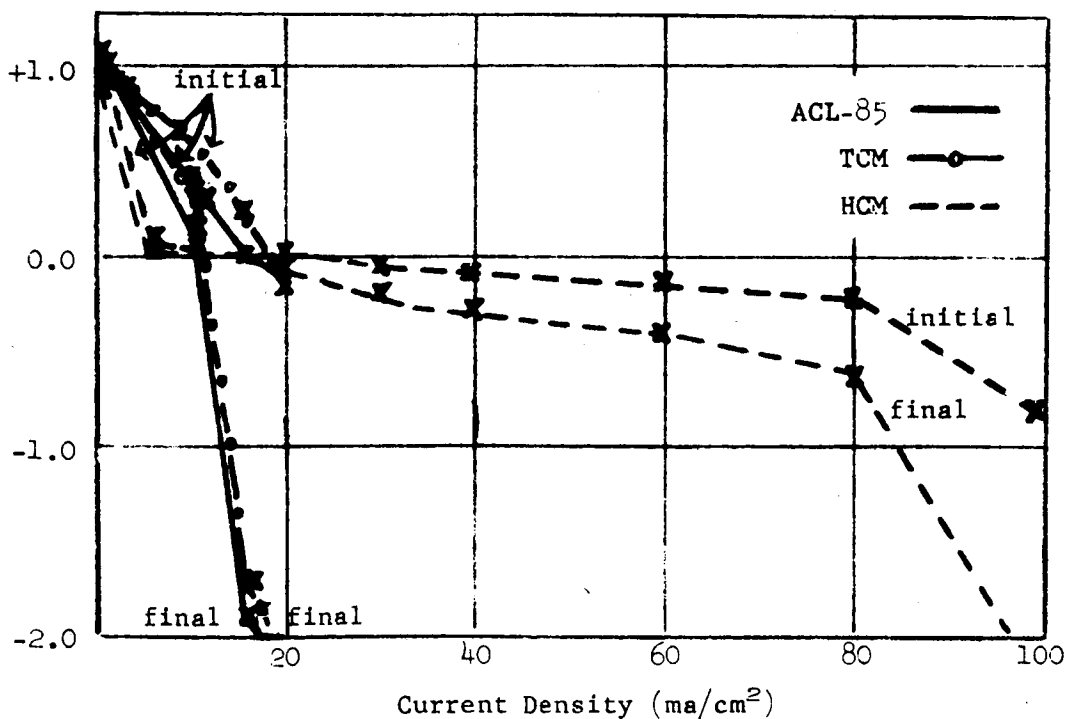
Cathode Voltage vs. Reference Electrode



\*  $\text{Li}$  appeared to be stable in the 0.1m HCM system but caused some electrolyte discoloration in the 0.1m ACL-85 system.

FIGURE 1l. A COMPARISON OF POSITIVE HALOGEN COMPOUNDS (1 MOLAL) IN  $\text{LiPF}_6$ -DIMETHYLFORMAMIDE (1 MOLAL). WORKING ELECTRODES - HP-10 SPEER CARBON ( $1\text{cm}^2$ ). COUNTER ELECTRODES -  $\text{Li}^{**}$ . REFERENCE ELECTRODES -  $\text{Ag}/\text{AgCl}$ .

Cathode Voltage vs. Reference Electrode



\*  $\text{Li}$  appeared to be stable in the 1.0m ACL-85 and 1.0m TCM systems but became covered with a white solid in the 1.0m HCM system.

FIGURE 1. ELECTROCHEMICAL HALF-CELL SCREENING OF DISSOLVED ACTIVE ORGANIC CATHODE MATERIALS (Continued)

FIGURE 1m. A COMPARISON OF POSITIVE HALOGEN COMPOUNDS (0.1 MOLAL) IN  $\text{LiPF}_6$ -DIMETHYLFORMAMIDE (1 MOLAL). WORKING AND COUNTER ELECTRODES - HP-10 SPEER CARBON ( $2\text{cm}^2$ ). REFERENCE ELECTRODES -  $\text{Ag}/\text{AgCl}$ .

Cathode Voltage vs. Reference Electrode

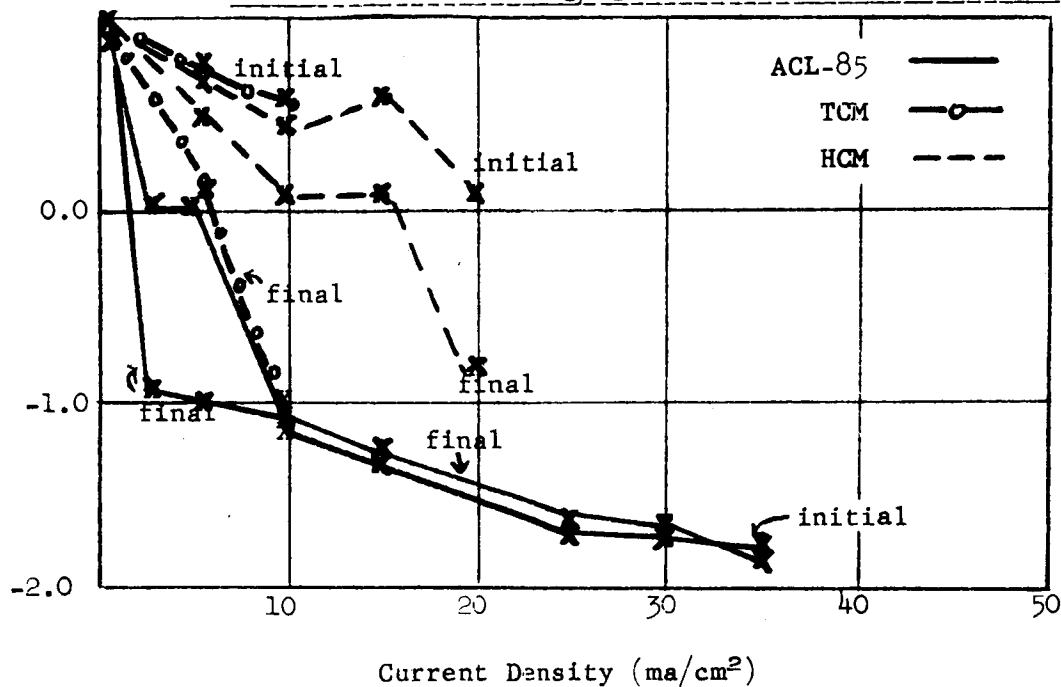


FIGURE 1n. A COMPARISON OF POSITIVE HALOGEN COMPOUNDS (1 MOLAL) IN  $\text{LiPF}_6$ -DIMETHYLFORMAMIDE (1 MOLAL). WORKING AND COUNTER ELECTRODES - HP-10 SPEER CARBON ( $2\text{cm}^2$ ). REFERENCE ELECTRODES -  $\text{Ag}/\text{AgCl}$ .

Cathode Voltage vs. Reference Electrode

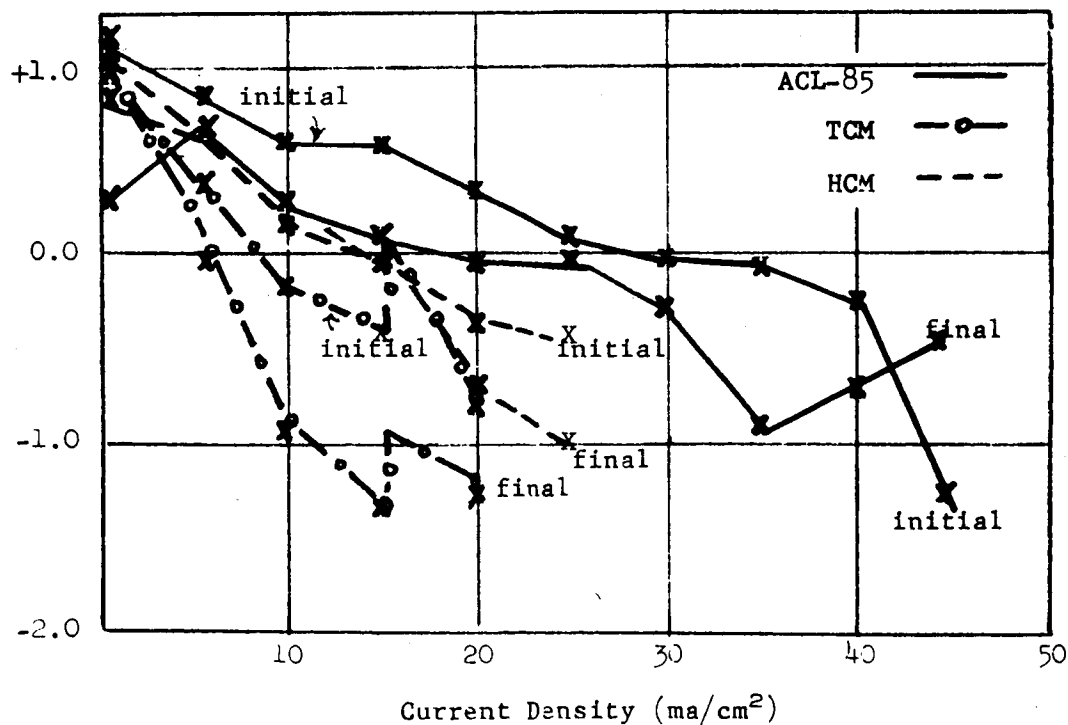


TABLE V. DENSITY AND VISCOSITY OF DISSOLVED ACTIVE ORGANIC CATHODE SOLUTIONS BEFORE AND AFTER ELECTROCHEMICAL HALF-CELL SCREENING TESTS

Active Cathode Material	Concentration (Molality)	Electrolyte	Working Electrode	Counter Electrode	Reference Electrode	Time of Measurement	Density* (g/cc)	Viscosity* (centi-poise)
1. MDB (see Fig. 1-a)	0.1	LiPF <sub>6</sub> -DMF	HP-10 Speer Carbon	HP-10 Speer Carbon	Ag/AgCl	Initial Final	1.059 1.059	1.83 1.80
2. MDB (see Fig. 1-a)	1.0	LiPF <sub>6</sub> -DMF	"	"	Ag/AgCl	Initial Final	1.098 1.098	2.14 2.22
3. ACL-85 (see Fig. 1-d)	0.1	LiPF <sub>6</sub> -DMF	"	"	Ag/AgCl	Initial Final	1.069 1.073	2.26 2.47
4. ACL-85 see Fig. 1-d	1.0	LiPF <sub>6</sub> -DMF	"	"	Ag/AgCl	Initial Final	1.175 Not Recorded	7.65**
5. ACL-85 (see Fig. 1-e)	1.0	LiPF <sub>6</sub> -DMF	"	"	Ag	Initial Final	1.177 1.170	6.50** 9.49***
6. TCM (see Fig. 1-g)	0.1	LiPF <sub>6</sub> -DMF	"	"	Ag/AgCl	Initial Final	1.065 1.064	2.10 2.11
7. TCM (see Fig. 1-g)	1.0(sat.)	LiPF <sub>6</sub> -DMF	"	"	Ag/AgCl	Initial Final	1.154 1.153	6.94 7.16
8. TCM (see Fig. 1-h)	0.1	LiPF <sub>6</sub> -NDA	"	"	Ag	Initial Final	1.121 1.120	2.14** 2.39***
9. HCM (see Fig. 1-j)	0.1	LiPF <sub>6</sub> -DMF	"	"	Ag/AgCl	Initial Final	1.068 1.076	3.30 2.23
10. HCM (see Fig. 1-j)	1.0(sat.)	LiPF <sub>6</sub> -DMF	"	"	Ag/AgCl	Initial Final	1.169 1.172	4.17** 5.45

\* Measured at 25°C.

\*\* Accuracy of the viscosity measurement was limited by a small amount of gas evolution in the solution at the time of measurement.

\*\*\* The solution was heterogeneous; therefore, density and viscosity measurements may be inaccurate.



TABLE VI. COULOMBIC EFFICIENCIES OF INORGANIC CATHODES

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TABLE VI. COULOMBIC EFFICIENCIES OF INORGANIC CATHODES

## A. Physical Details

Active Cathode Material	Method of Preparation	Anode	Electrolyte (1 molal)	Volume of electrolyte (ml)	Components Of Cathode After Discharge As Shown By X-ray Diffraction
1. $\text{CuF}_2$	A heptane slurry of $\text{CuF}_2$ (78 wt. %), Dixon graphite No. 200-43 (11 wt. %), and filter paper pulp (11 wt. %) was filtered on a Büchner funnel. The resulting porous mat was pressed at 15,000 lb/cm <sup>2</sup> on a 1cm <sup>2</sup> Ag matrix.	Li	LiCl-DMF	30	Not determined.
2. $\text{CuF}_2$	Same as No. 1.	Li	$(\text{C}_6\text{F}_5)(\text{CH}_3)_3\text{NPF}_6$ -IMF	*	Not determined.
3. $\text{CuF}_2$	Same as No. 1.	Li	$(\text{C}_6\text{F}_5)(\text{CH}_3)_3\text{NPF}_6$ -IMF	*	Not determined.
4. $\text{CuF}_2$	A small amount of $\text{CuF}_2$ on an Al expanded metal matrix (3/4" dia.) was placed in a die. The die was heated for 5 hours at 200°C in a N <sub>2</sub> purged tube furnace.	Li	Li <sub>10</sub> O <sub>4</sub> -PC	30	Cu, $\text{CuF}_2$ , Al**
5. $\text{CuF}_2$	A small amount of $\text{CuF}_2$ on a Cu screen (3/4" dia.) was placed in a die. The die was heated for 2 hours at 200°C in a N <sub>2</sub> purged tube furnace.	Li	Li <sub>2</sub> O <sub>4</sub> -PC	25	Cu**, $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$

\* Not measured.

\*\* Substrate metal.

TABLE VI. COULOMBIC EFFICIENCIES OF INORGANIC CATHODES (Continued)

## A. Physical Details (Continued)

Active Cathode Material	Method of Preparation	Anode	Electrolyte (1 mole/l.)	Volume of Electrolyte (ml)	Components Of Cathode After Discharge As Shown By X-ray Diffraction
6. CuF <sub>2</sub>	Same as No. 5.	Li	LiClO <sub>4</sub> -I	25	Cu*, CuF <sub>2</sub> ·2H <sub>2</sub> O, CuOHF, Cu(OH) <sub>2</sub>
7. CuF <sub>2</sub>	A small amount of CuF <sub>2</sub> on a Ag expanded metal matrix was placed in a die. The die was heated for 2 hours at 200°C in a N <sub>2</sub> purged tube furnace.	Li	LiClO <sub>4</sub> -I	25	Cu, CuF <sub>2</sub> , CuF <sub>2</sub> ·2H <sub>2</sub> O, Ag*
8. CuF <sub>2</sub>	Same as No. 7.	Li	LiClO <sub>4</sub> -I	25	Cu, CuF <sub>2</sub> , CuF <sub>2</sub> ·2H <sub>2</sub> O, Ag*
9. CuF <sub>2</sub>	A small amount of CuF <sub>2</sub> was hot-pressed on a Cu screen (3/4" dia.) in a metallurgical press at 8900 psi. Pressure was applied while the sample was heated to 150°C. The sample was cooled rapidly under pressure.	Li	LiClO <sub>4</sub> -I	25	Cu*, CuF <sub>2</sub> , CuF <sub>2</sub> ·2H <sub>2</sub> O
10. CuF <sub>2</sub>	Same as No. 9.	Li	LiClO <sub>4</sub> -C	25	Cu*, CuF <sub>2</sub> , CuF <sub>2</sub> ·2H <sub>2</sub> O
11. CuF <sub>2</sub>	Same as No. 9.	Li	LiClO <sub>4</sub> -C	3.2	Cu*, CuF <sub>2</sub>
12. CuF <sub>2</sub>	Same as No. 9. The CuF <sub>2</sub> was vacuum and N <sub>2</sub> dried prior to use.	Li	LiClO <sub>4</sub> -C	25	Cu*, CuF <sub>2</sub> , CuF <sub>2</sub> ·2H <sub>2</sub> O

\* Substrate metal.

TABLE VI. COULOMBIC EFFICIENCIES OF INORGANIC CATHODES (Continued)

## A. Physical Details (Continued)

Active Cathode Material	Method of Preparation	Anode	Electrolyte (1 m <sup>l</sup> )	Volume of Electrolyte (ml)	Components Of Cathode After Discharge As Shown By X-ray Diffraction
13. CuF <sub>2</sub>	Same as No. 9. The CuF <sub>2</sub> was vacuum and N <sub>2</sub> dried prior to use.	Li	LiCl 4-PC	25	Cu*, CuF <sub>2</sub> , CuF <sub>2</sub> ·2H <sub>2</sub> O
14. CuF <sub>2</sub>	Same as No. 9.	Li	LiCl 4-PC	25	Cu*, CuF <sub>2</sub> , CuF <sub>2</sub> ·2H <sub>2</sub> O
15. CuF <sub>2</sub>	Same as No. 9.	Li	LiCl 4-PC	25	Cu*, CuF <sub>2</sub> , CuF <sub>2</sub> ·2H <sub>2</sub> O
16. CuF <sub>2</sub>	Same as No. 9.	Li	LiCl 4-PC	2.5	X-ray data not yet available.
17. CuF <sub>2</sub>	Same as No. 9. The CuF <sub>2</sub> was vacuum and N <sub>2</sub> dried prior to use.	Li	LiCl 4-PC	25	Cu*, CuF <sub>2</sub> , CuF <sub>2</sub> ·2H <sub>2</sub> O
18. CuF <sub>2</sub>	Same as No. 9. The CuF <sub>2</sub> was vacuum and N <sub>2</sub> dried prior to use.	Li	LiCl 4-PC	25	Cu*, CuF <sub>2</sub> , CuF <sub>2</sub> ·2H <sub>2</sub> O
19. CuF <sub>2</sub>	A small amount of CuF <sub>2</sub> was hot-pressed on a Ag expanded metal screen (3/4" dia.) in a metallurgical press at 8900 psi. Pressure was applied while the sample was heated to 150°C. The sample was cooled rapidly under pressure.	Li	LiCl 4-PC	25	Cu, CuF <sub>2</sub> , CuF <sub>2</sub> ·2H <sub>2</sub> O, Ag*

\* Substrate metal.

A. Physical Details (Continued)

Active Cathode Material	Method of Preparation	Anode	Electrolyte (1 m <sup>l</sup> .al)	Volume of Electrolyte (ml)	Components Of Cathode After Discharge As Shown By X-ray Diffraction
20. CuF <sub>2</sub>	Same as No. 19.	Li	LiClO <sub>4</sub> -PC	25	Cu, CuF <sub>2</sub> , CuF <sub>2</sub> ·2H <sub>2</sub> O, Ag**
21. Ni(OH) <sub>2</sub>	A mixture of Ni(OH) <sub>2</sub> (80 wt.%), acetylene black (10 wt. %), and Solka-Floc (10 wt. %) was dry-pressed on a Cu screen (1cm <sup>2</sup> ) at a pressure of 10,000 lb. The electrode was 0.46mm thick.	Li	LiClO <sub>4</sub> -PC	*	X-ray data not yet available.
22. AgO	A mixture of AgO (95 wt. %) and Solka-Floc (5 wt. %) was dry-pressed on a Ag expanded metal matrix (1cm <sup>2</sup> ) at a pressure of 15,000 lb.	Li	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> NPF <sub>6</sub> -D F	30	Ag**
23. AgO	Same as No. 22. A No. 40 Whatman filter paper separator was used in the cell.	Li	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> NPF <sub>6</sub> -D F	2	Not determined.
24. V <sub>2</sub> O <sub>5</sub>	A mixture of V <sub>2</sub> O <sub>5</sub> (90 wt. %) and Solka-Floc (10 wt. %) was dry-pressed on a Cu screen (1cm <sup>2</sup> ) at a pressure of 10,000 lb.	Li	LiClO <sub>4</sub> -PC	*	Not determined.

\* Not measured.

\*\* Substrate metal.

TABLE VI. COULOMBIC EFFICIENCIES OF INORGANIC CATHODES (Continued)

## A. Physical Details (Continued)

Active Cathode Material	Method of Preparation	Anode	Electrolyte (1 molal)	Volume of Electrolyte (ml)	Components Of Cathode After Discharge As Shown By X-ray Diffraction
25. $V_2O_5$	A mixture of $V_2O_5$ (80 wt. %), acetylene black (10 wt. %), and Solka-Floc (10 wt. %) was dry-pressed on a Cu screen ( $1\text{cm}^2$ ) at a pressure of 10,000 lb.	Li	$LiClO_4\text{-PC}$	*	Not determined.

\* Not measured.

TABLE VI. COULOMBIC EFFICIENCIES OF INORGANIC CATHODES (Continued)

## B. Electrochemical Details

	Weight of Active Material (g)	Milli-equivalents	Average Current (ma)	Average Cell Voltage	Duration of Test (Minutes)	Coulombs		% Coulombic Efficiency
						Theoretical	Actual	
1.	0.2479	4.9	10.1	1.6	15	472.9	9.1	1.9
2.	0.0630	1.2	1.79	1.7	1560	115.8	167.5	*144.6**
3.	0.2102	4.1	9.2	0.9	1380	395.7	757.8	191.3**
4.	0.0498	0.98	1.6	1.7	550	94.6	51.5	54.5
5.	0.0603	1.2	2.15	1.4	314	114.8	40.6	35.3
6.	0.0513	1.0	10.2	0.9	29	97.5	17.8	18.3
7.	0.0515	1.0	2.49	1.4	249	97.5	37.2	38.1
8.	0.0485	0.96	10.0	0.9	49	92.6	29.4	31.7
9.	0.1194	2.4	1.76	1.6	900	226.8	95.0	41.9
10.	0.1583	3.1	1.71	1.3	1050	301.1	108.0	35.9
11.	0.1062	2.1	1.84	1.1	1072	201.7	118.3	58.7
12.	0.1921	3.8	1.88	1.1	480	365.7	54.2	14.8
***13.	0.0872	1.7	1.93	1.1	453	166.0	52.5	31.6
14.	0.0922	1.8	10.0	1.0	83	175.6	49.6	28.2
15.	0.2263	4.5	9.7	0.5	25	430.4	14.5	3.4
16.	0.1273	2.5	9.8	0.7	84	242.2	49.6	20.5

\* Test terminated before cut-off voltage of 0.2V for the cell was reached.

\*\* Apparently material other than  $\text{CuF}_2$  is contributing to the number of coulombs obtained.

\*\*\* Forced discharge.

TABLE VI. COULOMBIC EFFICIENCIES OF INORGANIC CATHODES (Continued)

B. Electrochemical Details (Continued)								
	Weight of Active Material (g)	Milli-equivalents	Average Current (ma)	Average Cell Voltage	Duration of Test (Minutes)	Coulombs		% Coulombic Efficiency
						Theoretical	Actual	
17.	0.1751	3.5	9.9	0.8	42	332.9	25.1	7.5
*18.	0.1265	2.5	9.8	0.8	41	240.3	24.2	10.1
19.	0.1101	2.2	2.14	1.4	697	209.4	89.5	42.7
20.	0.0911	1.8	10.0	0.9	66	172.7	39.7	23.0
21.	0.0450	0.97	1.5	1.2	221.9	95.6	20.0	21.4
22.	0.5338	8.67	1.79	1.6	13,140	836.7	1411.2	**168.7***
23.	0.0690	1.12	1.57	0.8	1350	108.1	127.2	117.7***
24.	0.2762	3.04	5	1.3	10	293.4	3.15	1.1*****
25.	0.0346	0.38	1.3	1.9	321	36.7	25.0	68.1*****

\* Forced discharge.

\*\* Test terminated before cut-off voltage of 0.2V for the cell was reached.

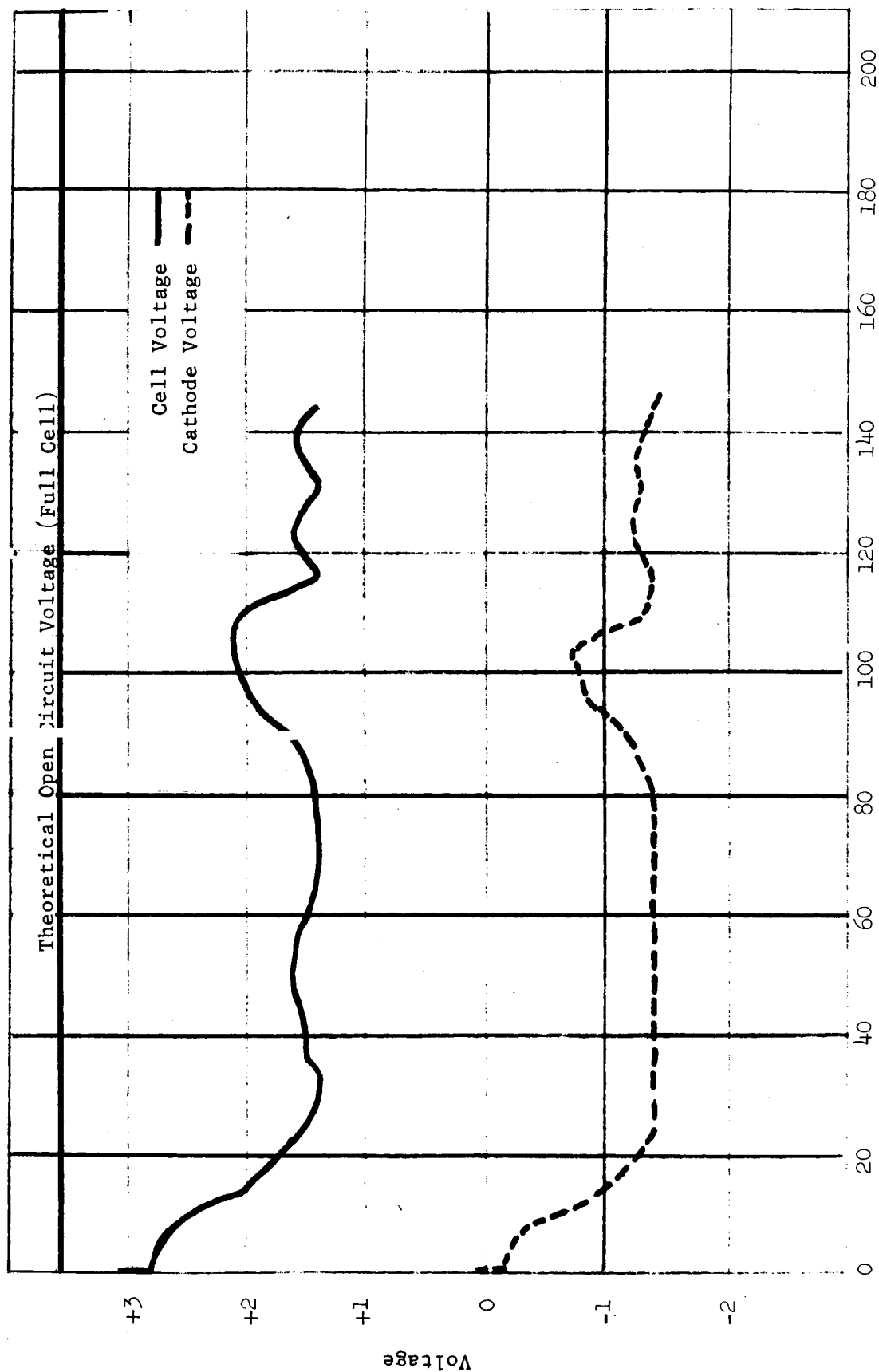
\*\*\* Apparently material other than  $\text{CuF}_2$  is contributing to the number of coulombs obtained.

\*\*\*\* Coulombic efficiency based on one electron change per V atom.



FIGURE 2. COULOMBIC EFFICIENCIES OF INORGANIC CATHODES: CATHODE VOLTAGE\*  
AND CELL VOLTAGE VS. % THEORETICAL COULOMBS

FIGURE 2a. CUPRIC FLUORIDE FILTER PAD CATHODE (AREA =  $1 \text{ cm}^2$ ) VS. LITHIUM IN N-PHENYL-N,N,N-TRIMETHYLAMMONIUM HEXAFLUOROPHOSPHATE-DIMETHYLFORMAMIDE. (NO. 2, TABLE VI) AVERAGE DISCHARGE CURRENT =  $1.79 \text{ ma}$ .



% Theoretical Coulombs

\* In Figure 2, all cathode voltages are vs. Ag/AgCl.

FIGURE 2. COULOMBIC EFFICIENCIES OF INORGANIC CATHODES: CATHODE VOLTAGE  
E VS. % THEORETICAL COULOMBS (Continued)

FIGURE 2b. CUPRIC FLUORIDE FILTER PAI CATHODE (AREA =  $1 \text{ cm}^2$ ) VS. LITHIUM IN N-PHENYL-N,N,N-TRI-METHYLAMMONIUM HEXAFLUOROPHOSPHATE-DIMETHYLFORMAMIDE. (NO. 3, TABLE VI). AVERAGE DISCHARGE CURRENT =  $9.2 \text{ ma}$ .

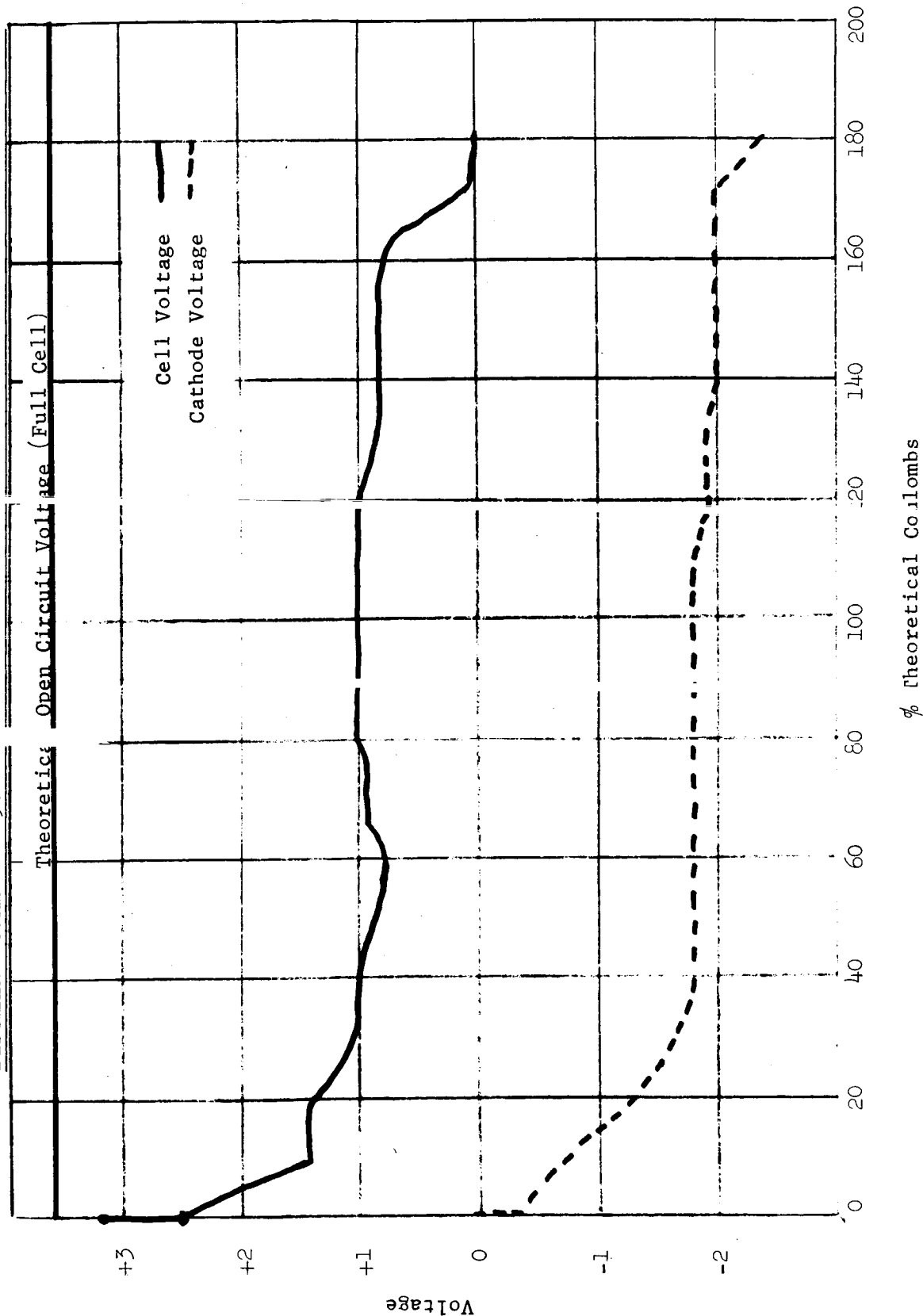


FIGURE 2. COULOMBIC EFFICIENCY OF INORGANIC CATHODES: CATHODE VOLTAGE AND CELL VOLTAGE VS. % THEORETICAL COULOMBS (Continued)

FIGURE 2c. CUPRIC FLUORIDE SINTERED ON ALUMINUM (AREA OF MATRIX =  $2.8\text{cm}^2$ ) VS. LITHIUM IN  $\text{LiClO}_4$ -PROPYLENE CARBONATE. (0.4, TABLE VI). AVERAGE DISCHARGE CURRENT =  $1.6\text{ma}$ .

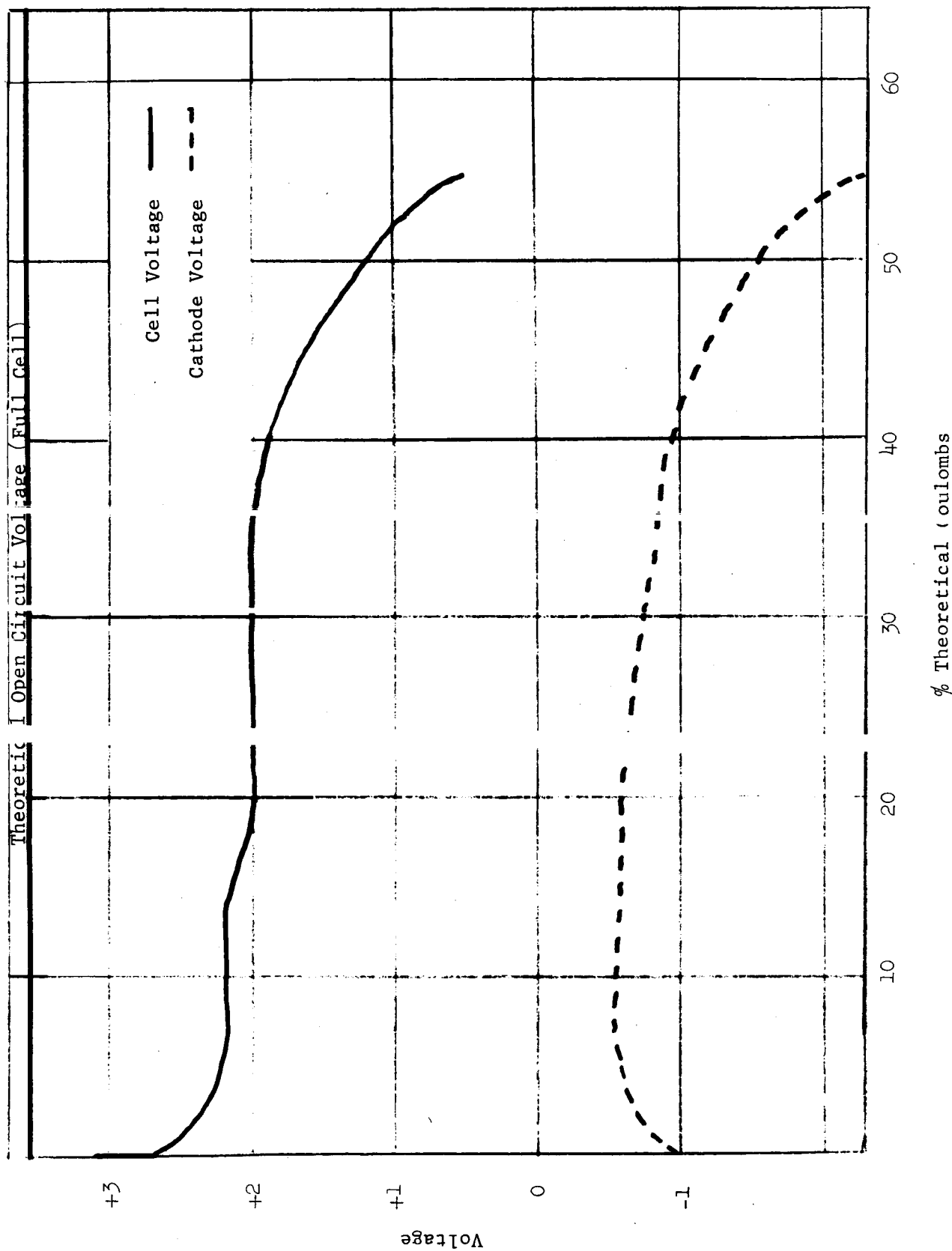


FIGURE 2. COULOMBIC EFFICIENCIES OF INORGANIC CATHODES: CATHODE VOLTAGE AND CELL VOLTAGE VS. % THEORETICAL COULOMBS (Continued)

FIGURE 2d. CUPRIC FLUORIDE SINTERED ON COPPER (AREA OF MATRIX =  $2.8\text{cm}^2$ ) VS. LITHIUM IN  $\text{LiClO}_4$ -PROPYLENE CARBONATE. (NO. 5, TABLE VI). AVERAGE DISCHARGE CURRENT =  $2.15\text{ma}$ .

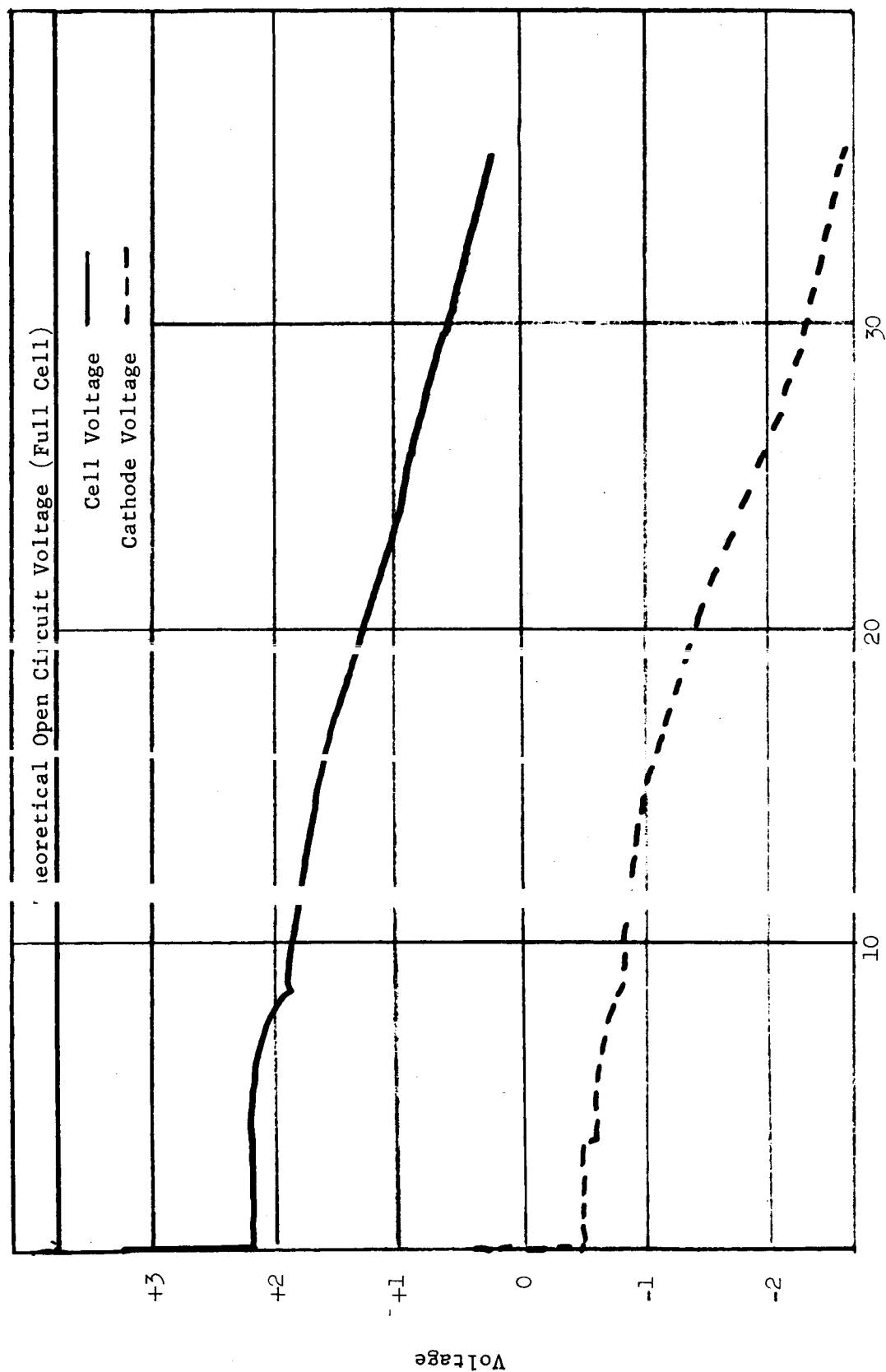


FIGURE 2. COULOMBIC EFFICIENCIES OF INORGANIC CATHODES: CATHODE VOLTAGE AND CELL VOLTAGE VS. % THEORETICAL COULOMBS (Continued)

FIGURE 2e. CUPRIC FLUORIDE SINTERED ON COPPER (AREA OF MATRIX =  $2.8\text{cm}^2$ ) VS. LITHIUM IN  $\text{LiClO}_4$ -PROPYLENE CARBONATE. (NO. 6, TABLE VI). AVERAGE DISCHARGE CURRENT =  $10.2\text{ma}$ .

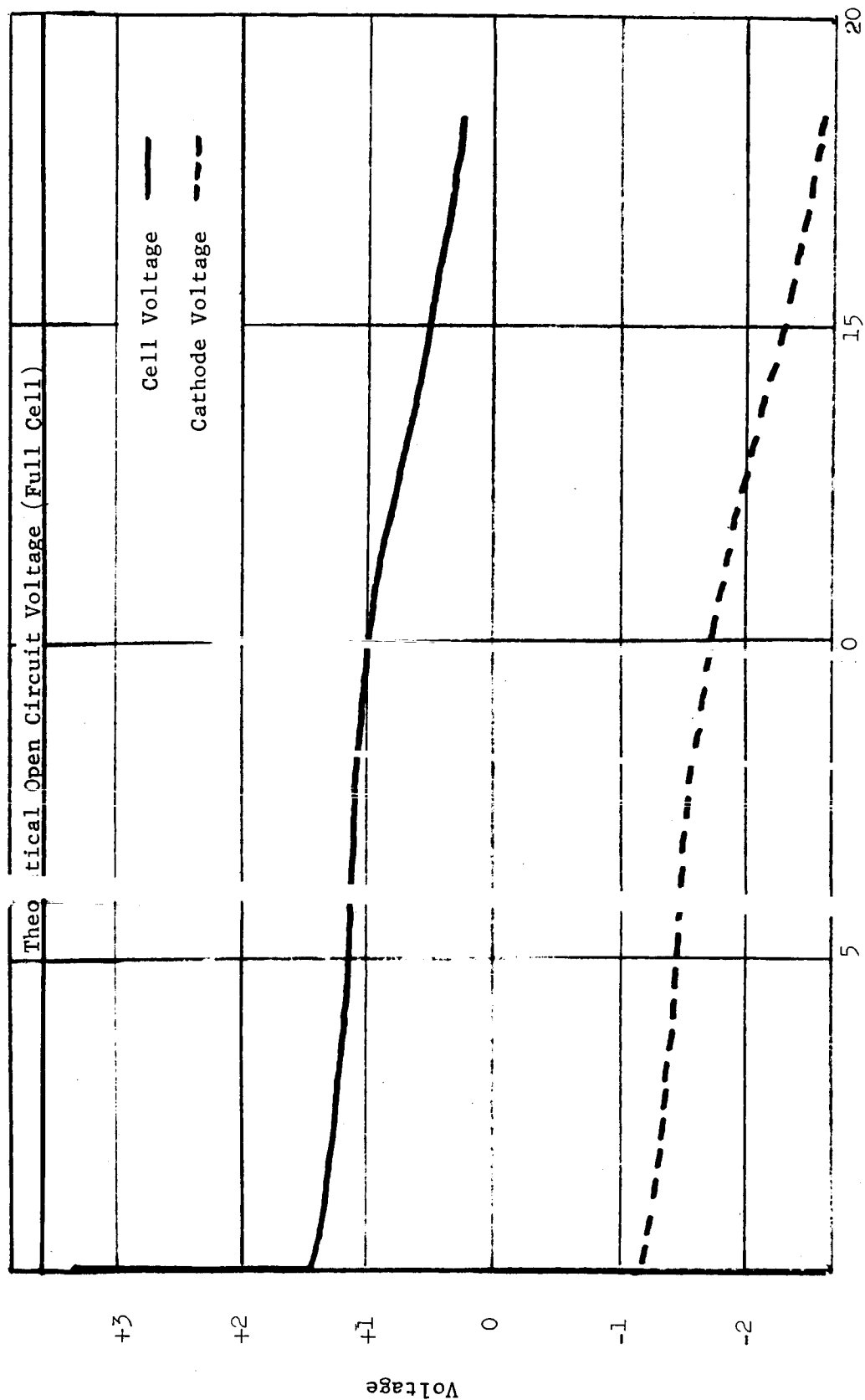


FIGURE 2. COULOMBIC EFFICIENCIES OF INORGANIC CATHODES: CATHODE VOLTAGE AND CELL VOLTAGE VS. % THEORETICAL COULOMBS (Continued)

FIGURE 2f. CUPRIC FLUORIDE SINTERED ON SILVER (AREA OF MATRIX =  $2.8\text{cm}^2$ ) VS. LITHIUM IN  $\text{LiClO}_4$ -PROPYLENE CARBONATE. (NO. 7, TABLE VI). AVERAGE DISCHARGE CURRENT =  $2.49\text{ma}$ .

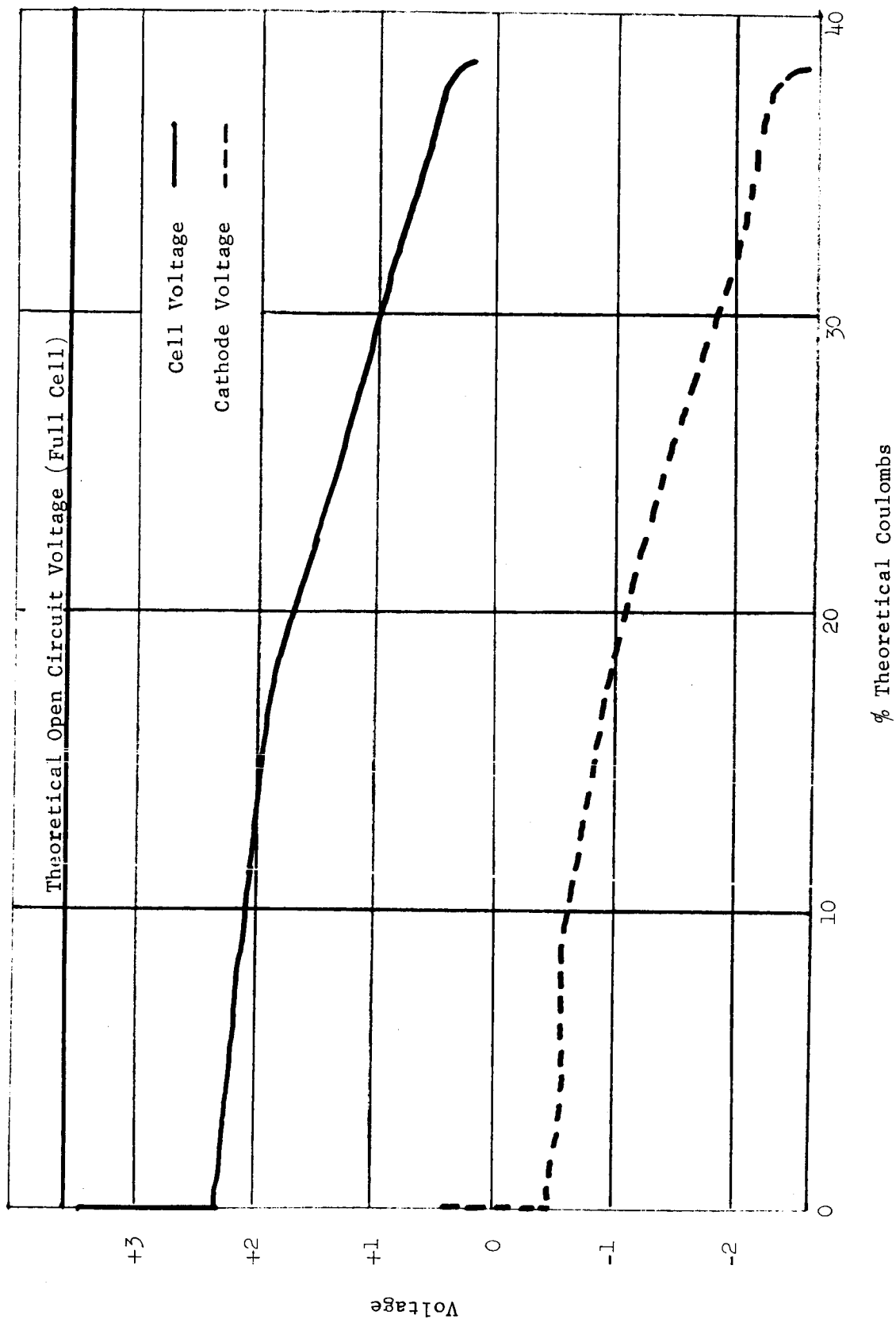


FIGURE 2. COULOMBIC EFFICIENCIES OF INORGANIC CATHODES: CATHODE VOLTAGE AND CELL VOLTAGE VS. % THEORETICAL COULOMBS (Continued)

FIGURE 2g. CUPRIC FLUORIDE SINTERED ON SILVER (AREA OF MATRIX =  $2.8\text{cm}^2$ ) VS. LITHIUM IN  $\text{LiClO}_4$ -PROPYLENE CARBONATE. (NO. 8, TABLE VI). AVERAGE DISCHARGE CURRENT =  $10.0\text{ma}$ .

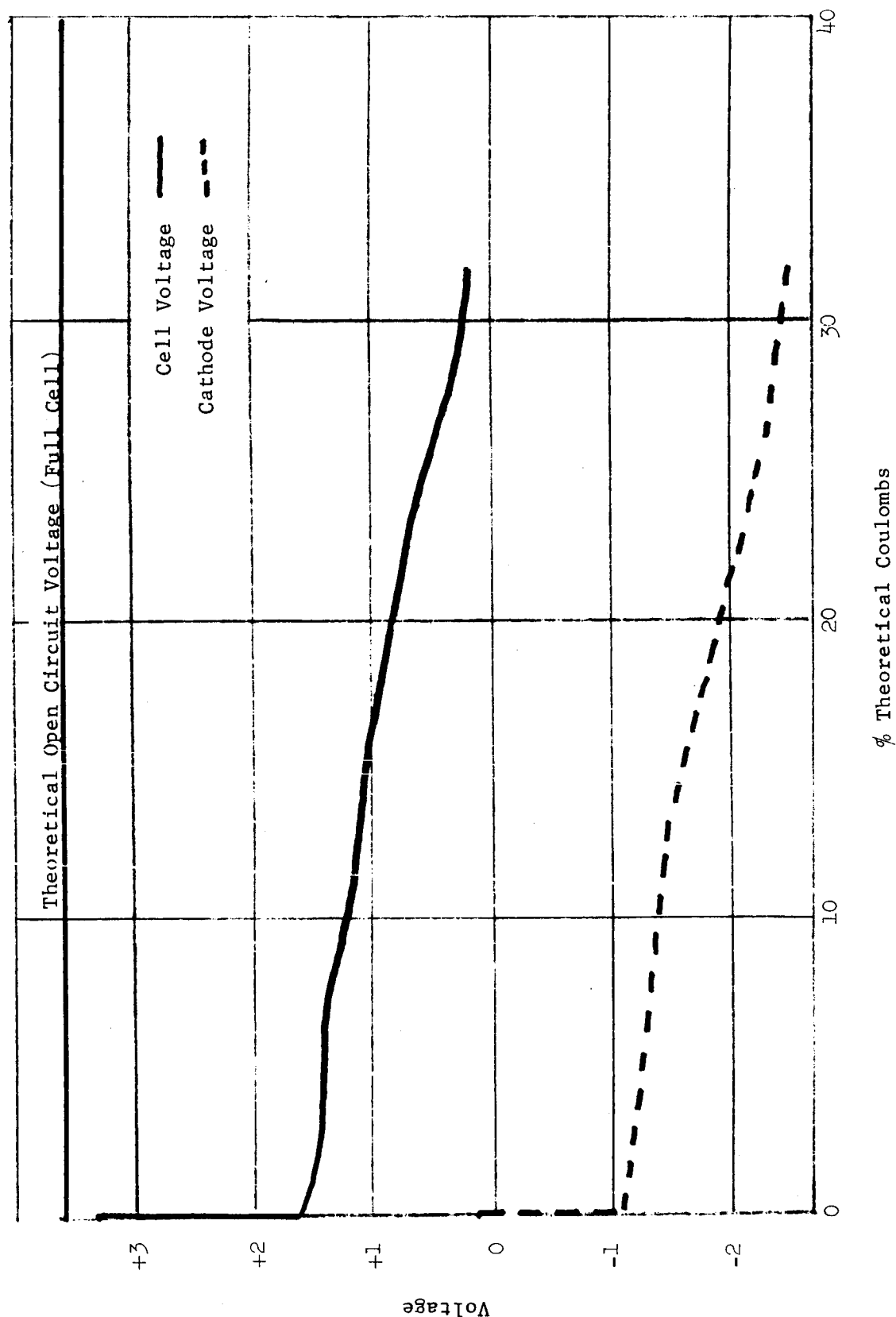


FIGURE 2. COULOMBIC EFFICIENCIES OF INORGANIC CATHODES: CATHODE VOLTAGE AND CELL VOLTAGE VS. % THEORETICAL COULOMBS (Continued)

FIGURE 2h. CUPRIC FLUORIDE SINTERED ON COPPER (AREA OF MATRIX =  $2.8\text{cm}^2$ ) VS. LITHIUM IN  $\text{LiClO}_4$ -PROPYLENE CARBONATE. (NO. 2, TABLE VI). AVERAGE DISCHARGE CURRENT =  $1.76\text{ma}$ .

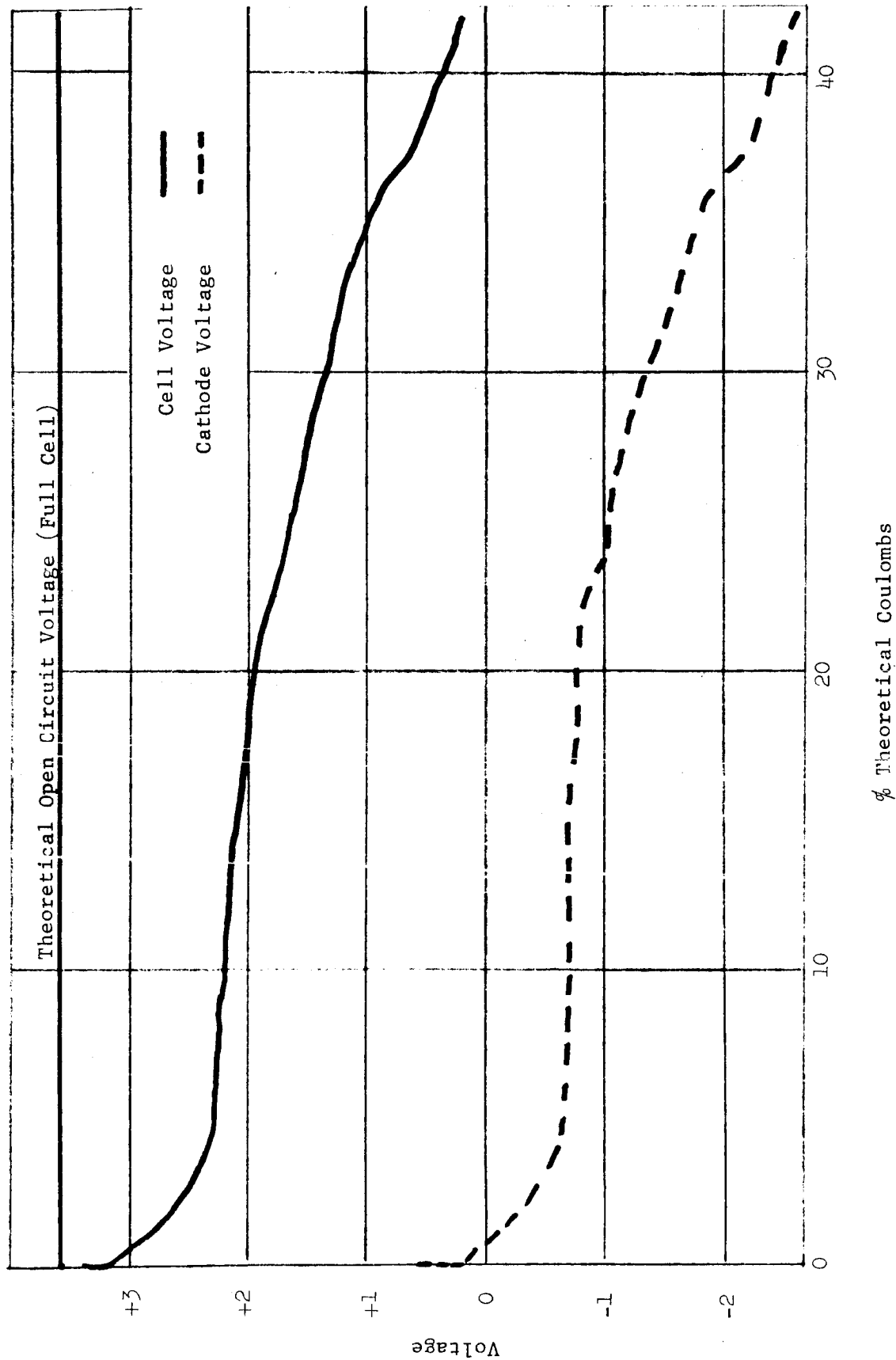
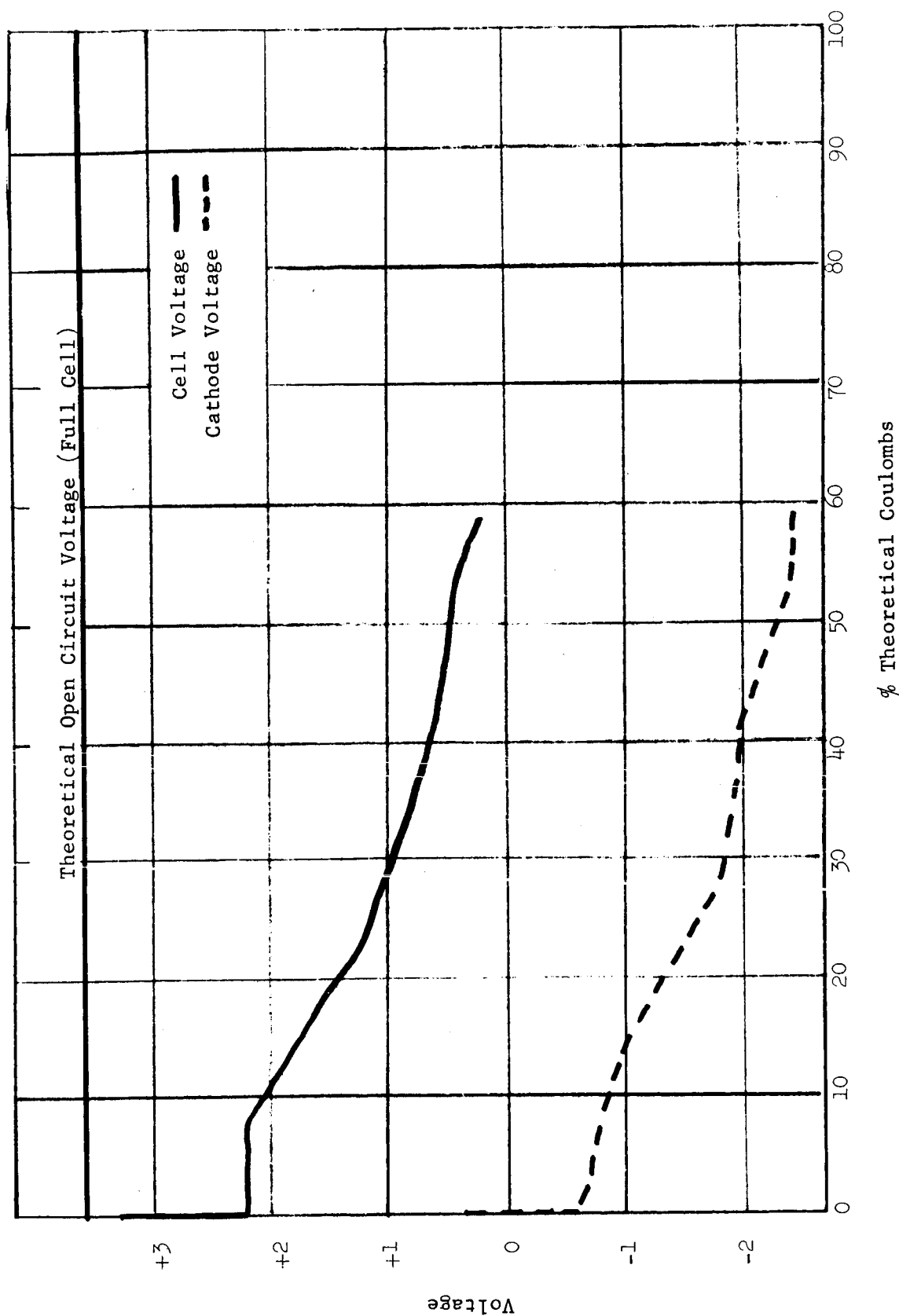




FIGURE 2. COULOMBIC EFFICIENCIES OF INORGANIC CATHODES: CATHODE VOLTAGE AND CELL VOLTAGE VS. % THEORETICAL COULOMBS (Continued)

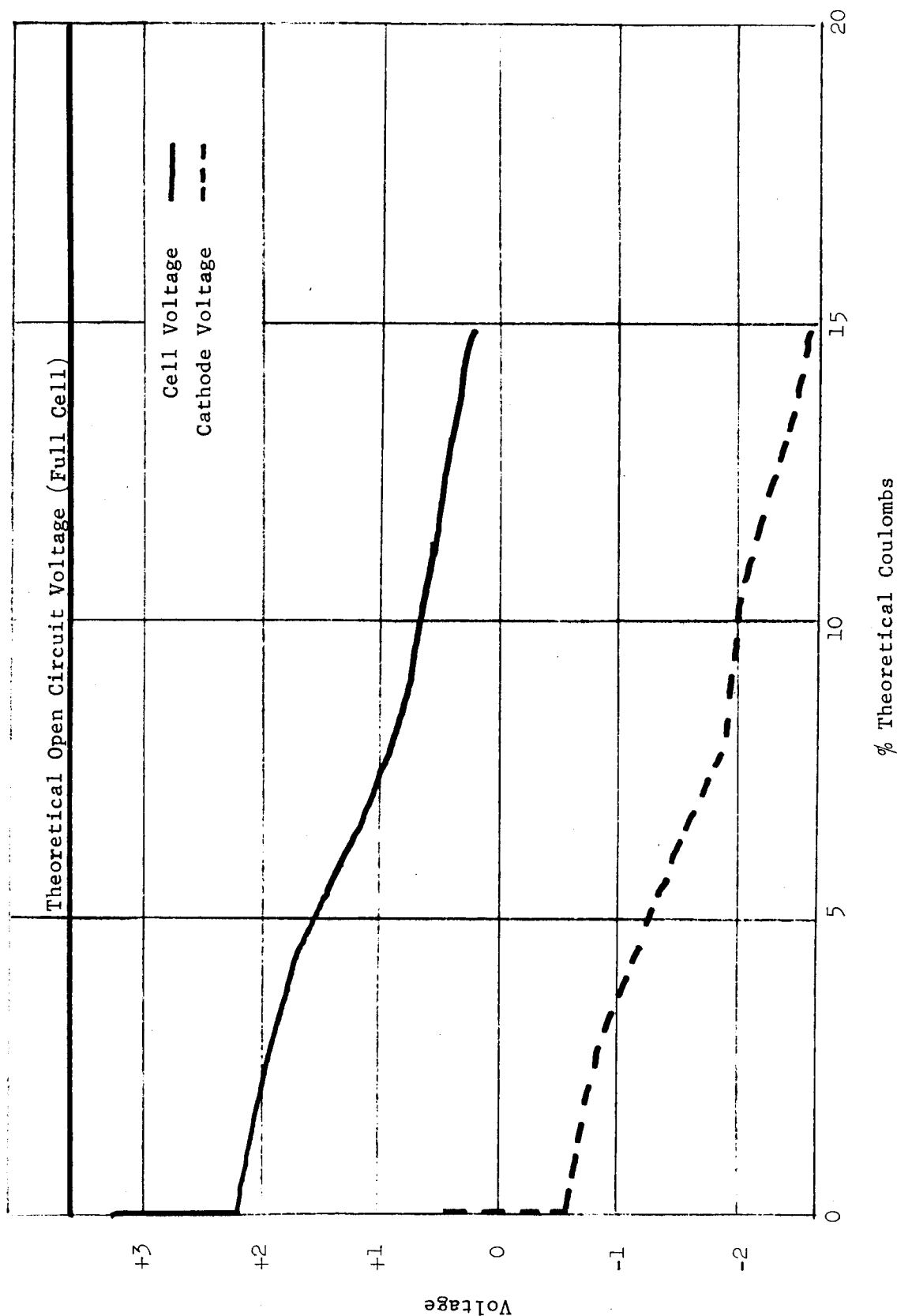
FIGURE 2i. CUPRIC FLUORIDE SINTERED ON COPPER (AREA OF MATRIX =  $2.8\text{cm}^2$ ) VS. LITHIUM IN  $\text{LiClO}_4$ -PROPYLENE CARBONATE\*. (NO. 11, TABLE VI). AVERAGE DISCHARGE CURRENT =  $1.84\text{ma}$ .



\* A minimal amount of electrolyte (3.2ml) was utilized.

FIGURE 2. COULOMBIC EFFICIENCIES OF INORGANIC CATHODES: CATHODE VOLTAGE AND CELL VOLTAGE VS. % THEORETICAL COULOMBS (Continued)

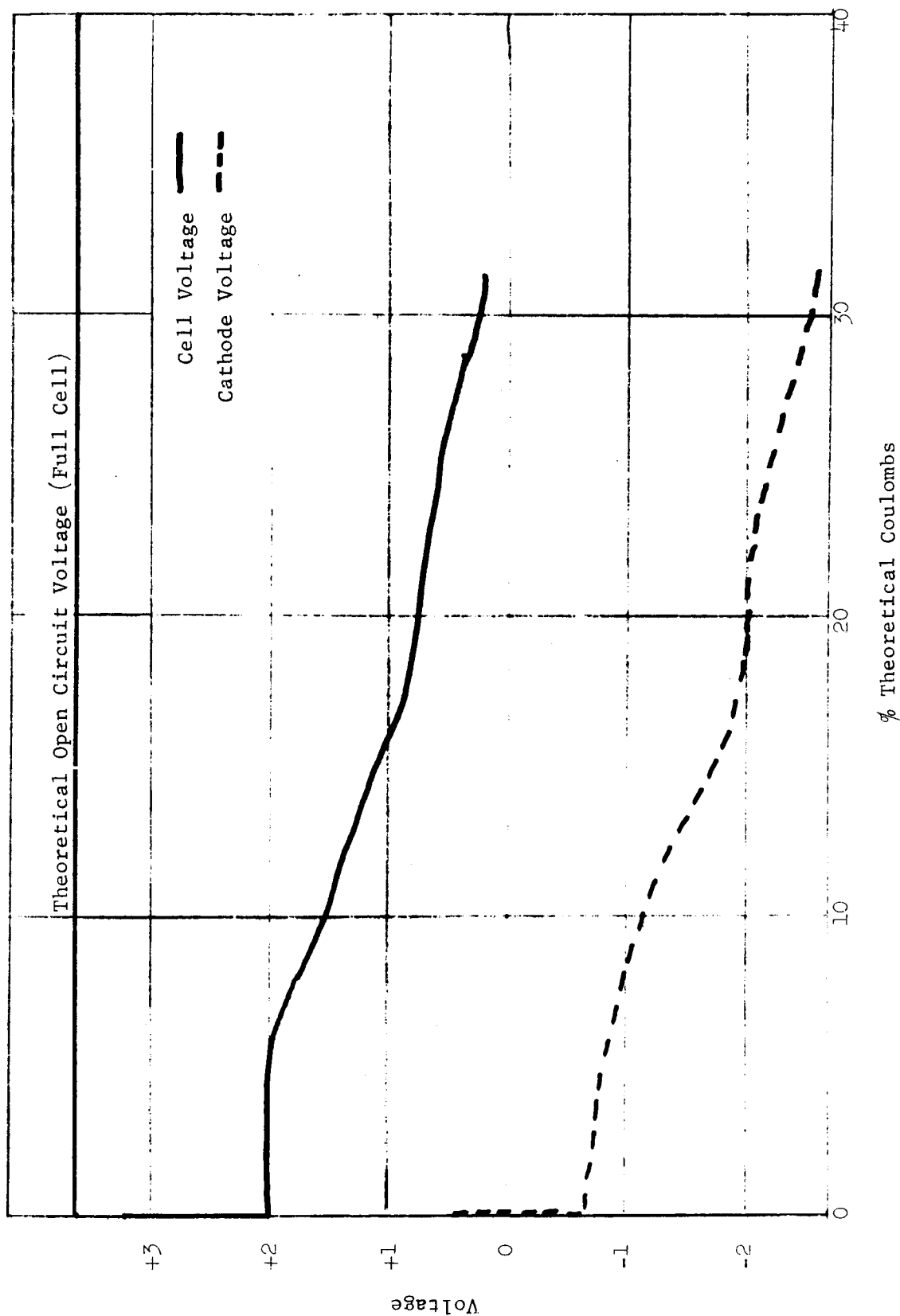
FIGURE 2j. CUPRIC FLUORIDE\* SINTERED ON COPPER (AREA OF MATRIX =  $2.8\text{cm}^2$ ) VS. LITHIUM IN  $\text{LiClO}_4$ -PROPYLENE CARBONATE. (NO. 12, TABLE VI). AVERAGE DISCHARGE CURRENT =  $1.88\text{ma}$ .



\* The  $\text{CuF}_2$  was vacuum and nitrogen-dried prior to sintering.

FIGURE 2. COULOMBIC EFFICIENCIES OF INORGANIC CATHODES: CATHODE VOLTAGE AND CELL VOLTAGE VS. % THEORETICAL COULOMBS (Continued)

FIGURE 2k. CUPRIC FLUORIDE\* SINTERED ON COPPER (AREA OF MATRIX =  $2.8\text{cm}^2$ ) VS. LITHIUM IN  $\text{LiClO}_4$ -PROPYLENE CARBONATE. (NO. 13, TABLE VI). AVERAGE DISCHARGE CURRENT\*\* =  $1.93\text{ma}$ .



\* The  $\text{CuF}_2$  was vacuum and nitrogen-dried prior to sintering.  
 \*\* Forced discharge.

FIGURE 2. COULOMBIC EFFICIENCIES OF INORGANIC CATHODES: CATHODE VOLTAGE AND CELL VOLTAGE VS. % THEORETICAL COULOMBS (Continued)

FIGURE 21. CUPRIC FLUORIDE SINTERED ON COPPER (AREA OF MATRIX =  $2.8\text{cm}^2$ ) VS. LITHIUM IN  $\text{LiClO}_4$ -PROPYLENE CARBONATE. (NO. 14, TABLE VI). AVERAGE DISCHARGE CURRENT =  $10.0\text{ma}$ .

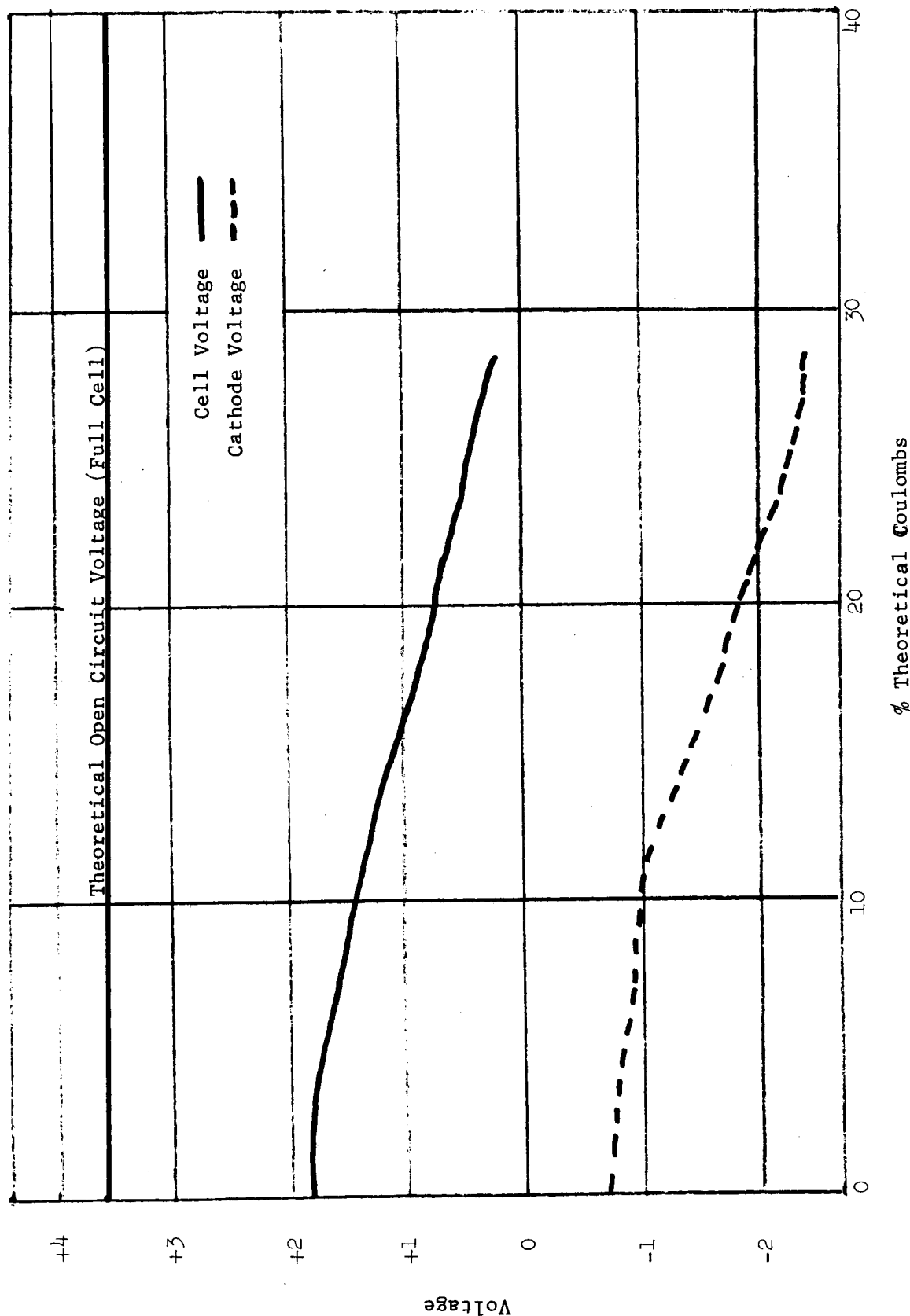
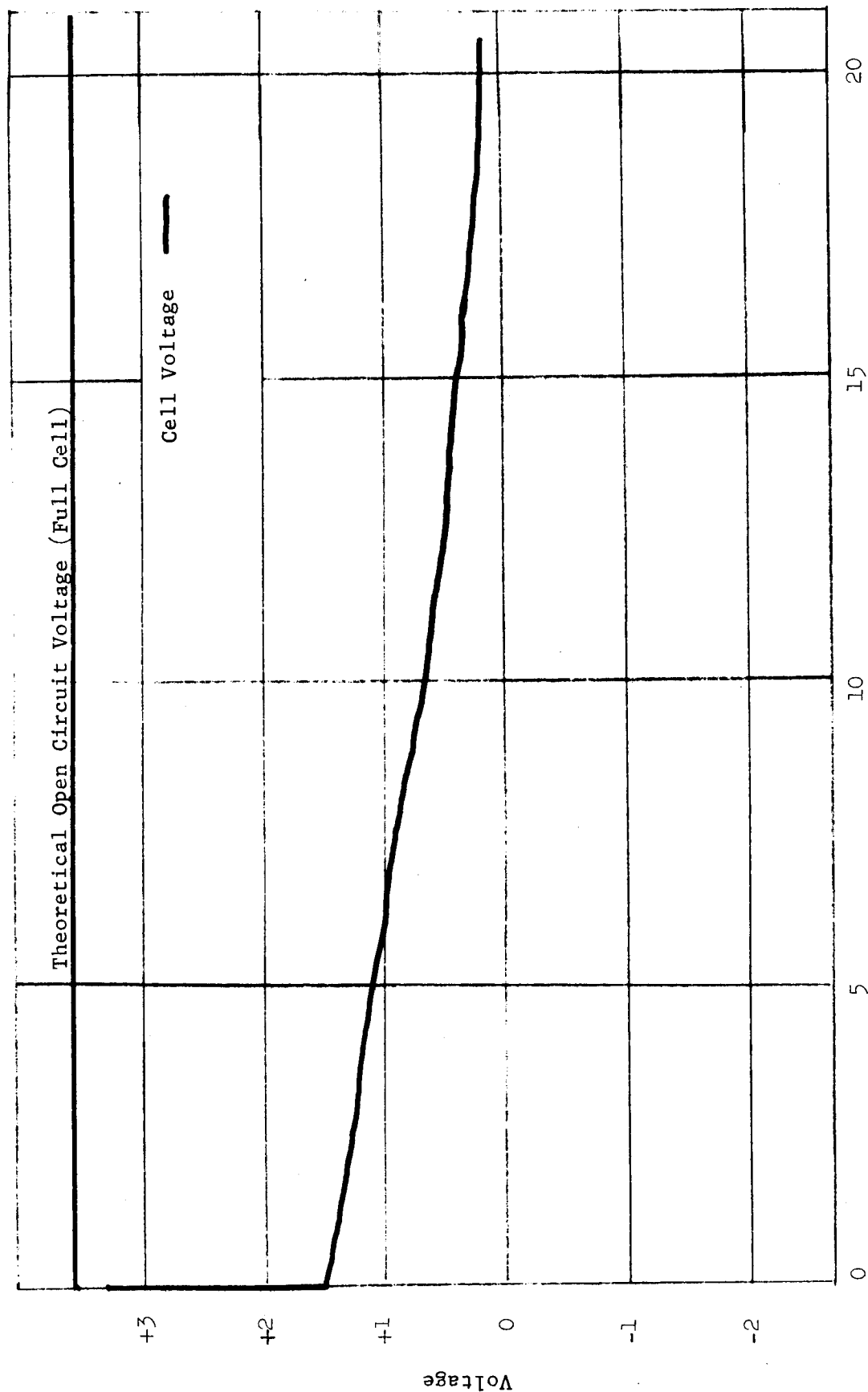


FIGURE 2. COULOMBIC EFFICIENCIES OF INORGANIC CATHODES: CATHODE VOLTAGE\*  
AND CELL VOLTAGE VS. % THEORETICAL COULOMBS (Continued)

FIGURE 2m. CUPRIC FLUORIDE SINTERED ON COPPER (AREA OF MATRIX =  $2.8\text{cm}^2$ ) VS. LITHIUM IN  
 $\text{LiClO}_4$ -PROPYLENE CARBONATE\*\*. (NO. 16, TABLE VI). AVERAGE DISCHARGE  
CURRENT =  $9.8\text{ma}$ .



% Theoretical Coulombs

\* Mechanical failure of the recorder invalidated the cathode voltage reading for this test.

\*\* A minimal amount of electrolyte ( $2.5\text{ml}$ ) was utilized.

FIGURE 2. COULOMBIC EFFICIENCIES OF INORGANIC CATHODES: CATHODE VOLTAGE AND CELL VOLTAGE VS. % THEORETICAL COULOMBS (Continued)

FIGURE 2n. CUPRIC FLUORIDE SINTERED ON SILVER (AREA OF MATRIX =  $2.8\text{cm}^2$ ) VS. LITHIUM IN  $\text{LiClO}_4$ -PROPYLENE CARBONATE. (NO. 19, TABLE VI). AVERAGE DISCHARGE CURRENT =  $2.14\text{ma}$ .

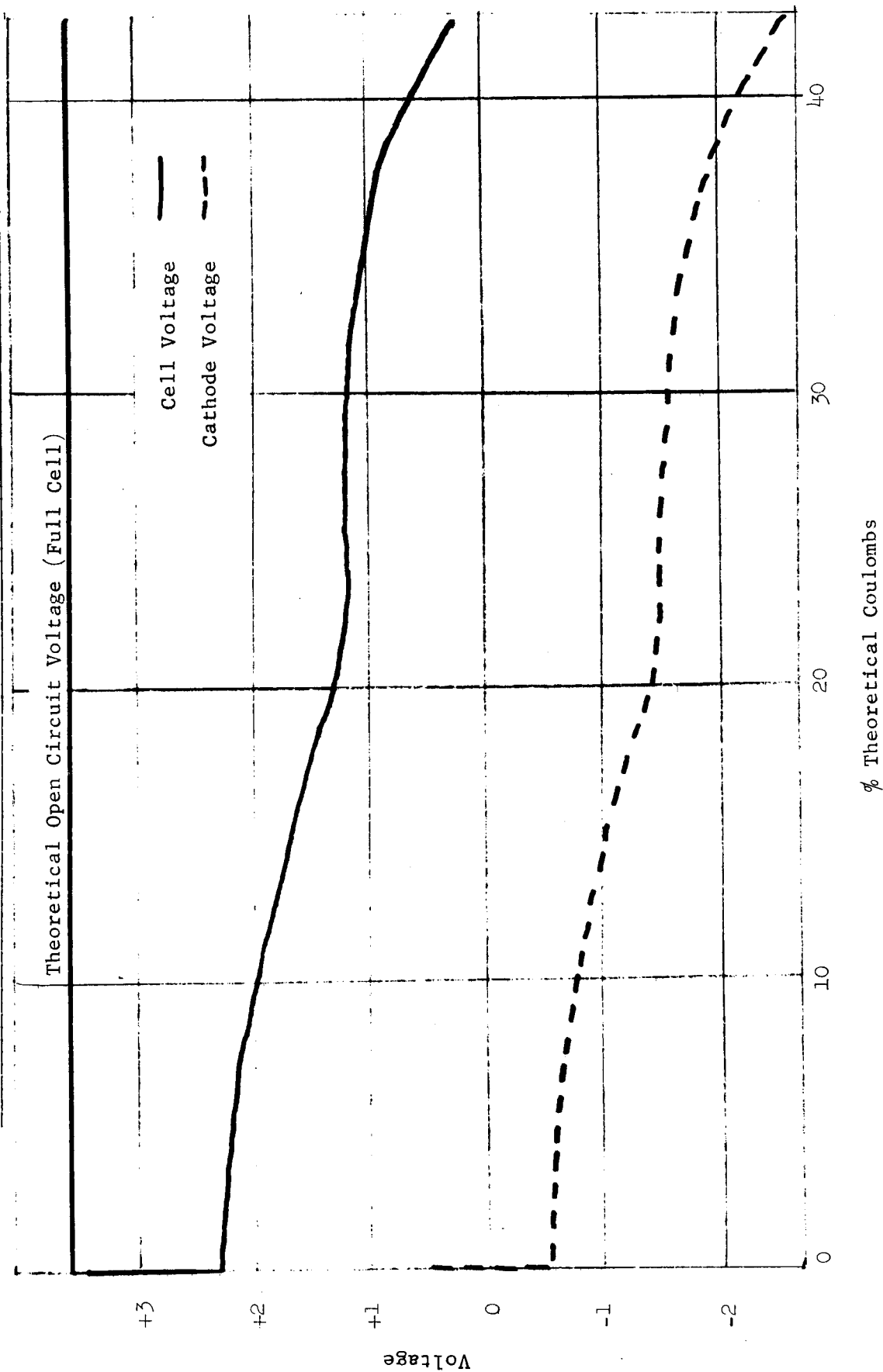


FIGURE 2. COULOMBIC EFFICIENCIES OF INORGANIC CATHODES: CATHODE VOLTAGE AND CELL VOLTAGE VS. % THEORETICAL COULOMBS (Continued)

FIGURE 2o. CUPRIC FLUORIDE SINTERED ON SILVER (AREA OF MATRIX =  $2.8\text{cm}^2$ ) VS. LITHIUM IN  $\text{LiClO}_4$ -PROPYLENE CARBONATE. (NO. 20, TABLE VI). AVERAGE DISCHARGE CURRENT = 10.0ma.

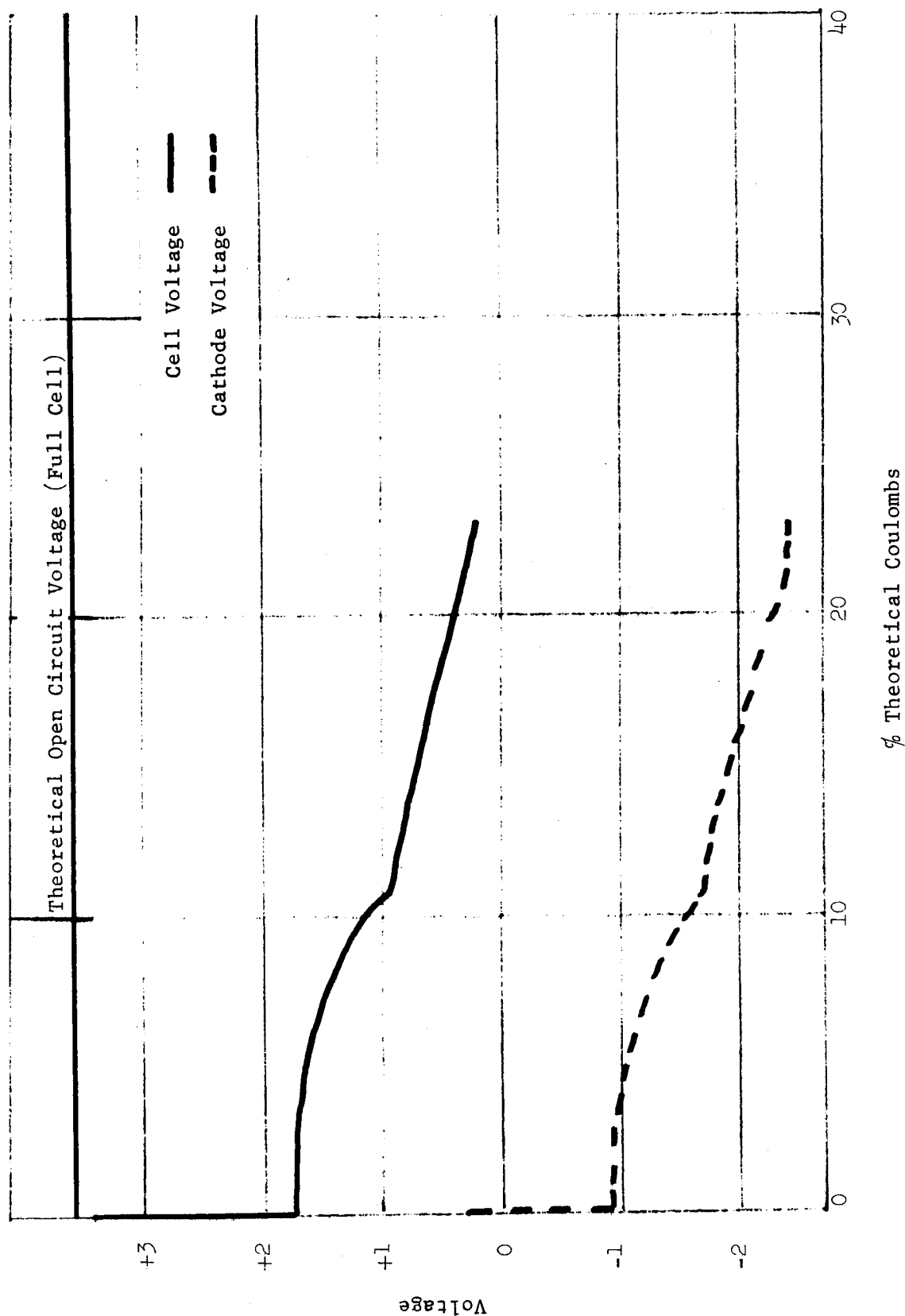


FIGURE 2. COULOMBIC EFFICIENCIES OF INORGANIC CATHODES: CATHODE VOLTAGE AND CELL VOLTAGE VS. % THEORETICAL COULOMBS (Continued)

FIGURE 2p. NICKEL HYDROXIDE (AREA OF MATRIX =  $1\text{cm}^2$ ) VS. LITHIUM IN  $\text{LiClO}_4$ -PROPYLENE CARBONATE. (NO. 21, TABLE VI). AVERAGE DISCHARGE CURRENT =  $1.5\text{ma}$ .

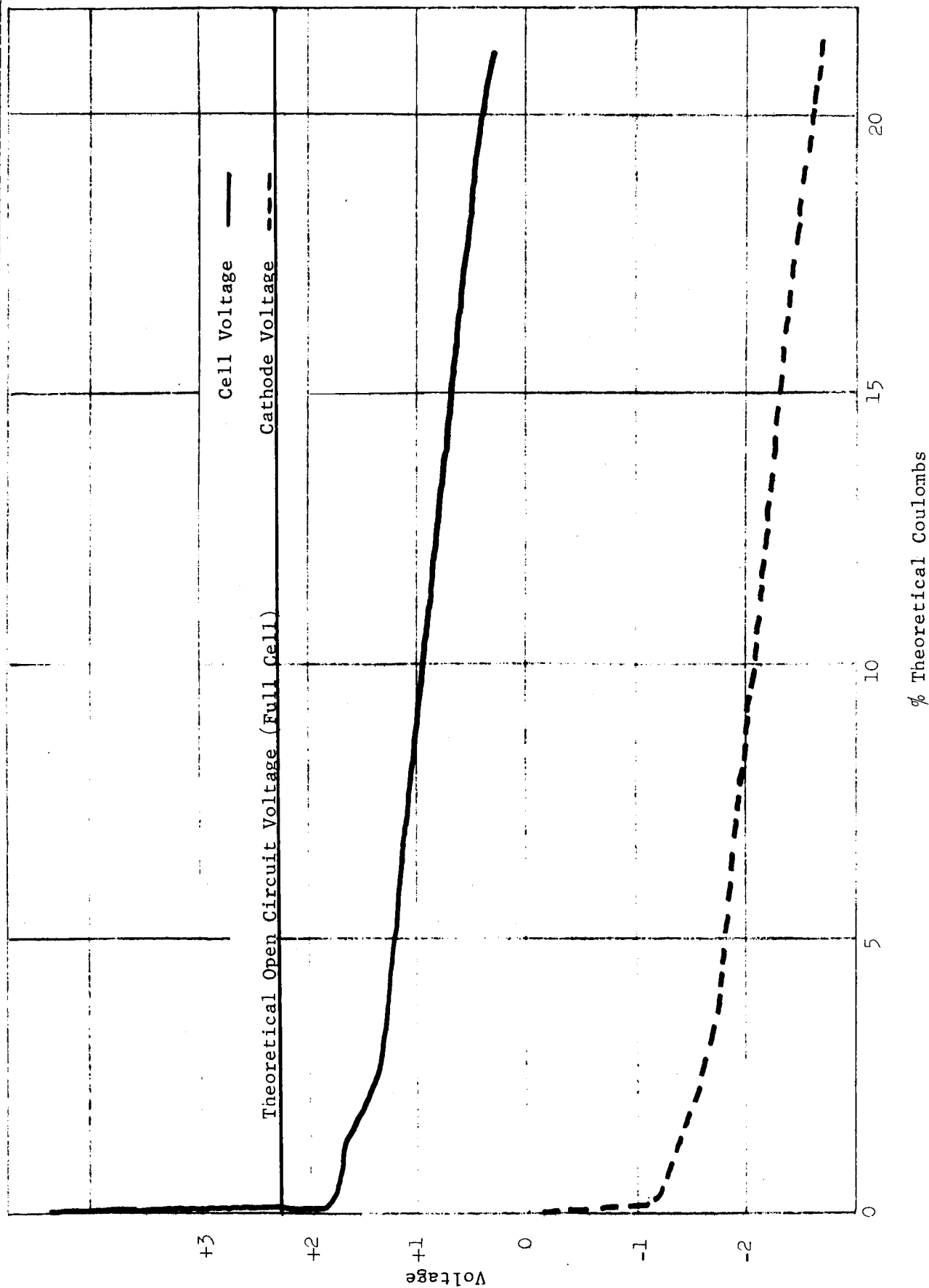
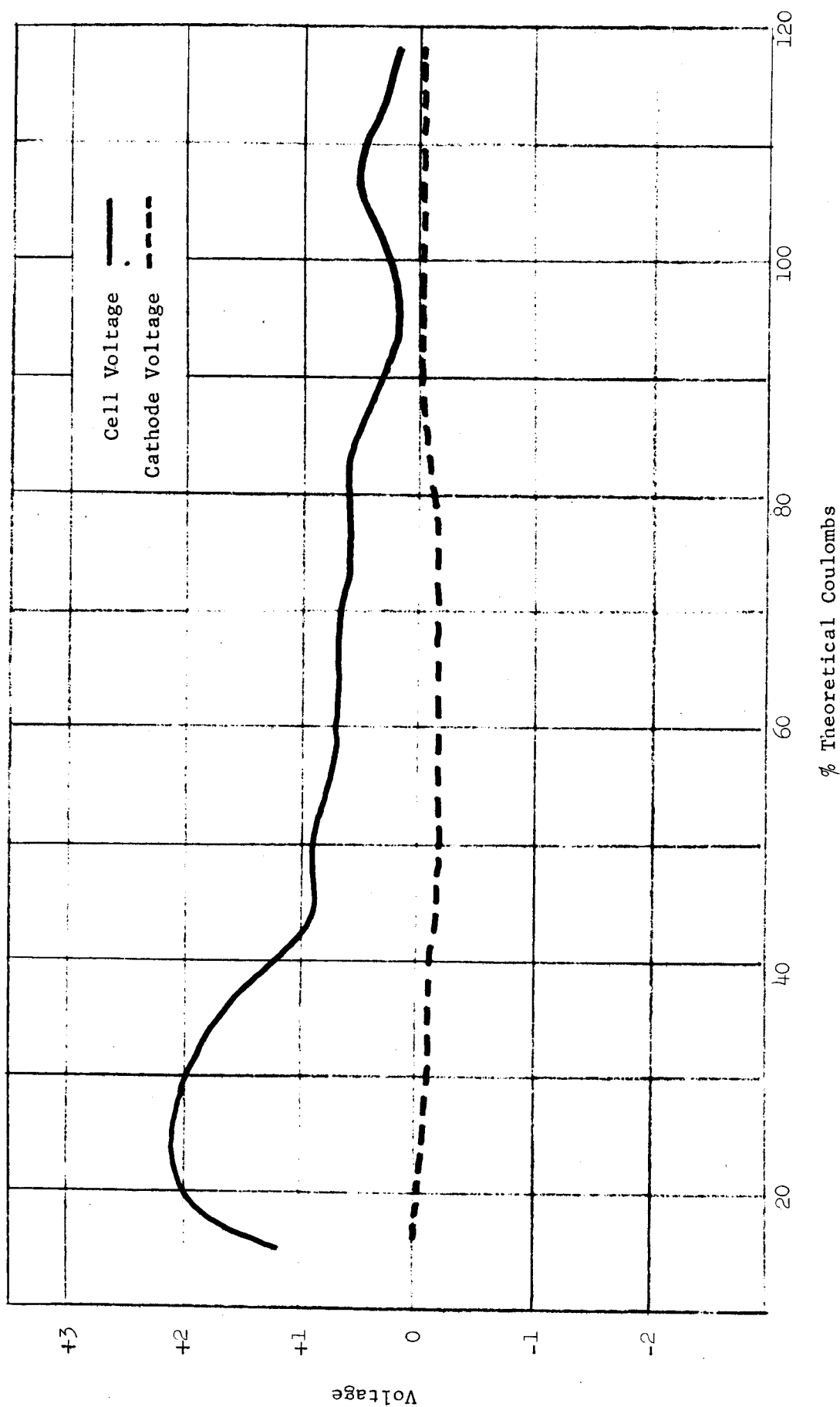




FIGURE 2. COULOMBIC EFFICIENCIES OF INORGANIC CATHODES: CATHODE VOLTAGE AND CELL VOLTAGE VS. % THEORETICAL COULOMBS (Continued)

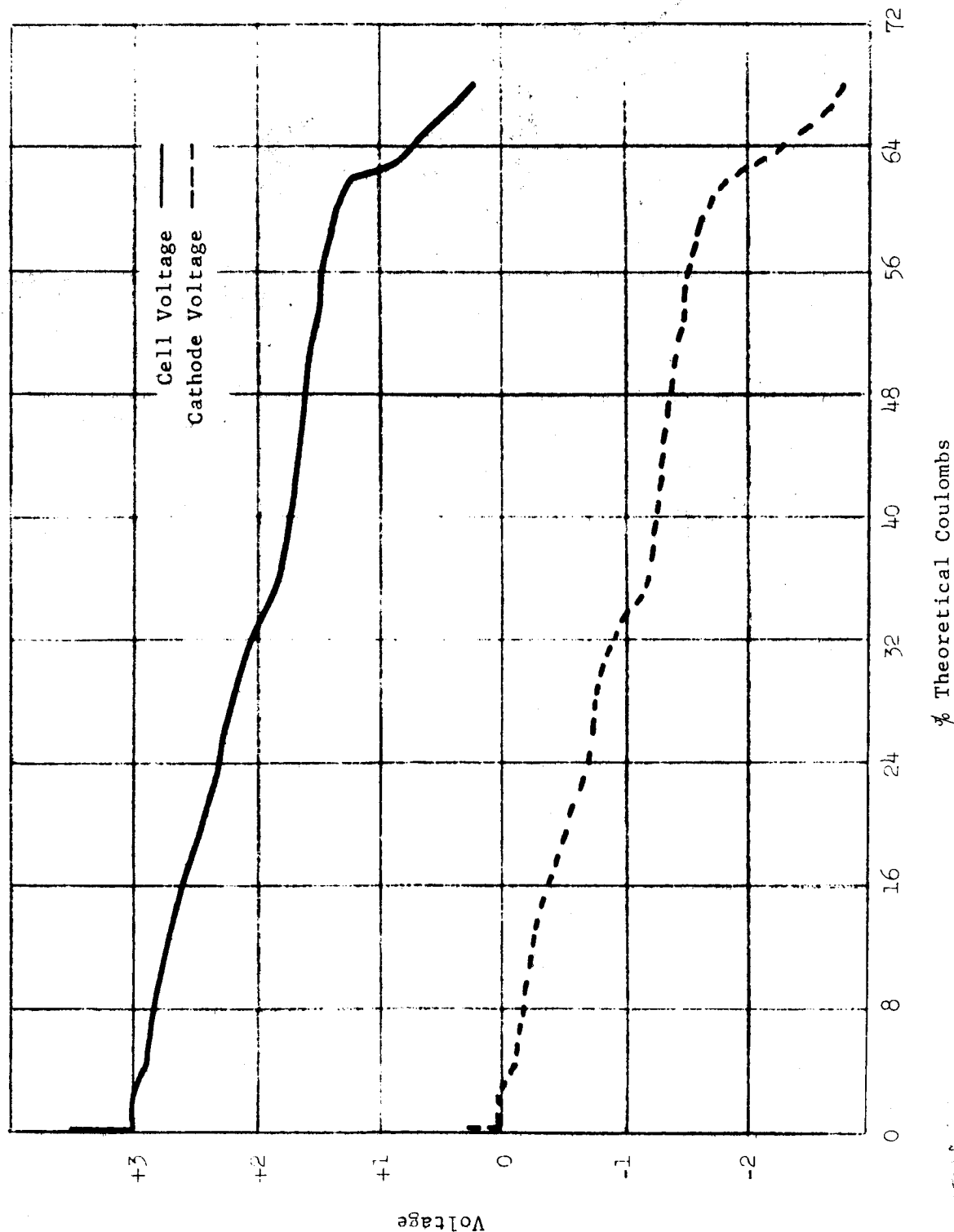
FIGURE 2q. SILVER OXIDE (AREA OF MATRIX =  $0.5\text{cm}^2$ ) VS. LITHIUM IN N-PHENYL-N,N,N-TRIMETHYLANMONIUM HEXAFLUOROPHOSPHATE-DIMETHYLFORMAMIDE\*. (NO. 23, TABLE VI). AVERAGE DISCHARGE CURRENT =  $1.57\text{ma}$ .



\* A No. 40 Whatman filter paper separator was used for this discharge.

FIGURE 2. COULOMBIC EFFICIENCIES OF INORGANIC CATHODES: CATHODE VOLTAGE AND CELL VOLTAGE, VS. % THEORETICAL COULOMBS\* (Continued)

FIGURE 2r. VANADIUM PENTOXIDE (AREA OF MATRIX =  $1\text{cm}^2$ ) VS. LITHIUM IN  $\text{LiClO}_4$ -PROPYLENE CARBONATE. (NO. 25, TABLE VI). AVERAGE DISCHARGE CURRENT =  $1.3\text{ma}$ .



\* Based on a one electron change per V atom.

FIGURE 3. COULOMBIC EFFICIENCIES OF DISSOLVED ACTIVE ORGANIC CATHODE MATERIALS:  
 ACL-85 (0.01 MOLAL) IN LiPF<sub>6</sub>-N-NITROSODIMETHYLAMINE. LITHIUM COUNTER  
 ELECTRODES - HP-10 SPEER CARBON WORKING ELECTRODES (AREA = 2cm<sup>2</sup>). Ag  
 REFERENCE ELECTRODES.

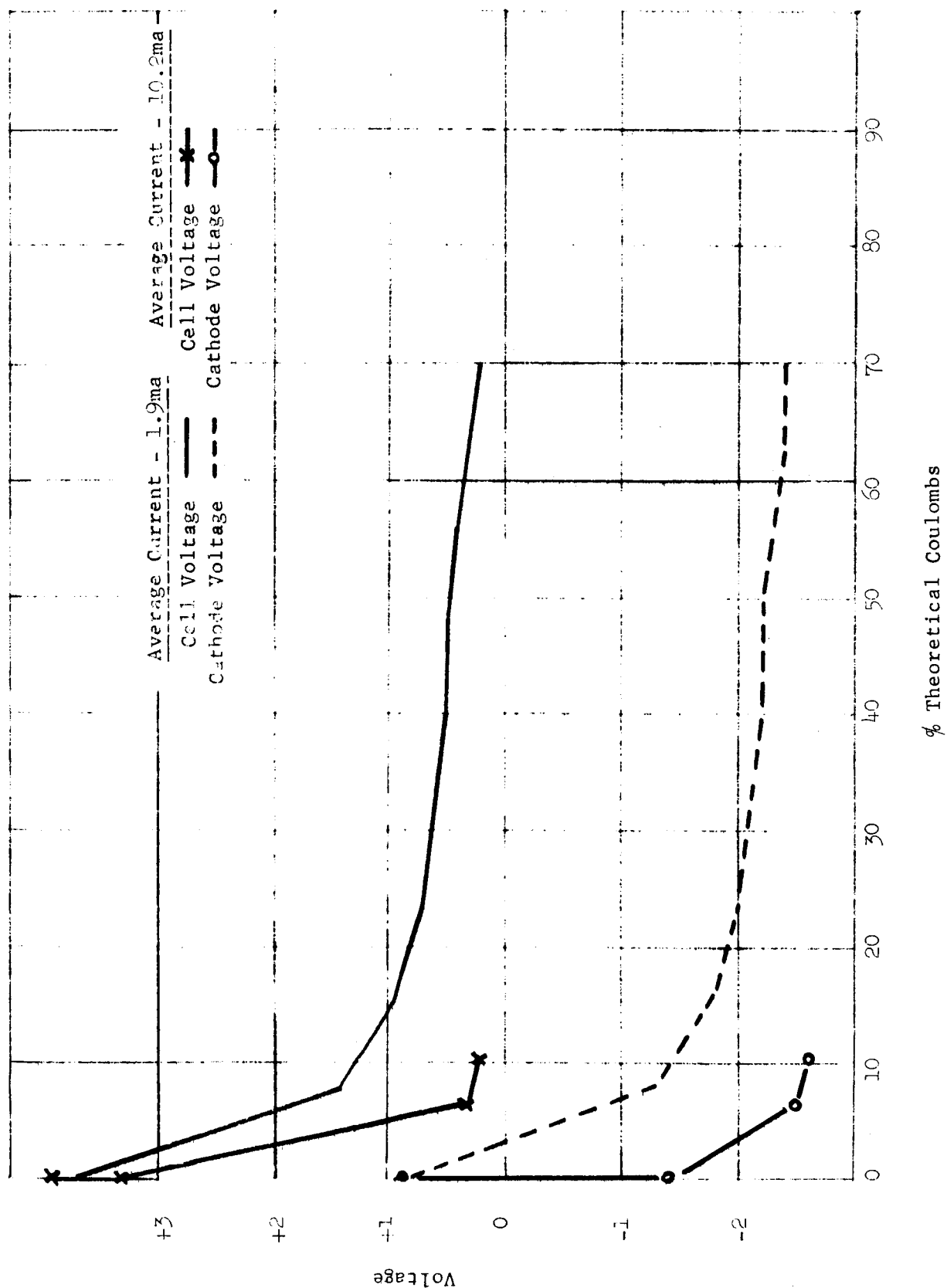
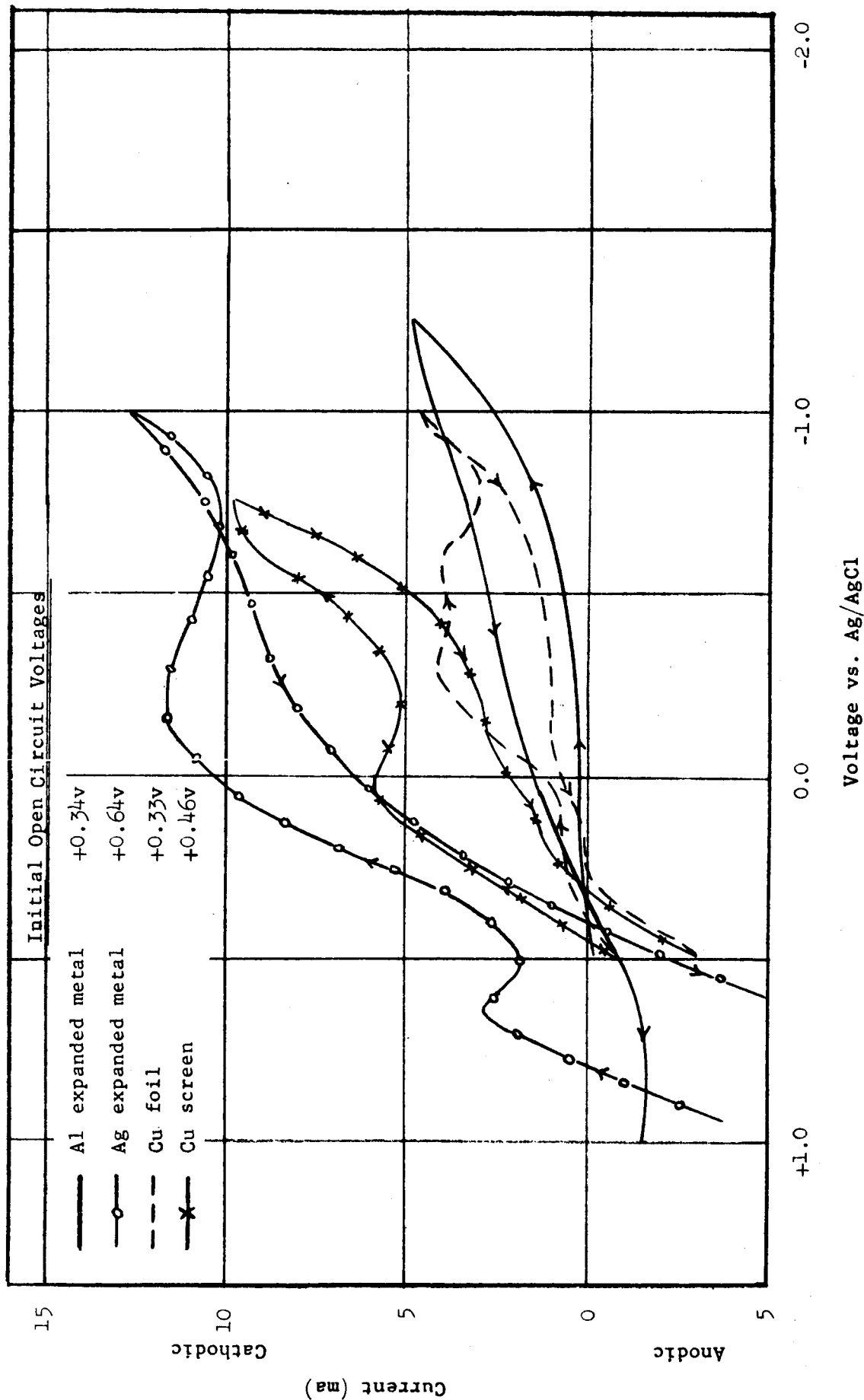


FIGURE 4. LINEARLY VARYING POTENTIAL STUDIES  
OF INORGANIC CATHODES

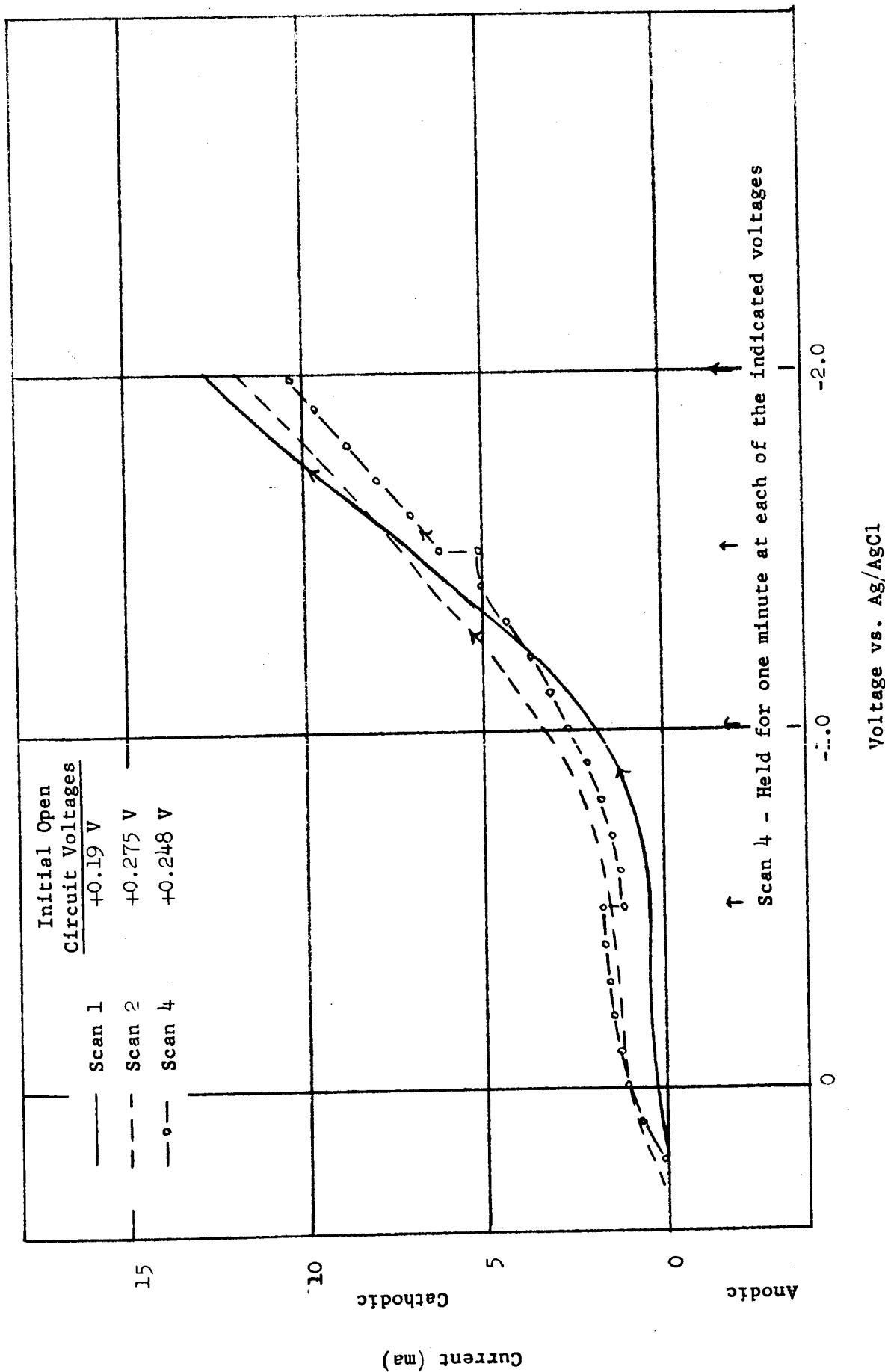
<u>Cathode</u>	<u>Electrolyte (1 molal)</u>	<u>Page</u>
a. Cupric Fluoride Sintered in a Nitrogen Atmosphere on a Variety of Substrates.	LiClO <sub>4</sub> - Propylene Carbonate	IV-62
b. Cupric Fluoride Sintered in a Nitrogen Atmosphere on Aluminum.	LiClO <sub>4</sub> - Propylene Carbonate	IV-63
c. Cupric Fluoride Sintered in a Metallurgical Press on Silver.	LiPF <sub>6</sub> - N-Nitrosodimethylamine	IV-64
d. Cupric Fluoride Thin Films Formed on Copper Foil by Solvent Evaporation and by Electrolysis of 48% Hydrogen Fluoride.	LiClO <sub>4</sub> - Propylene Carbonate	IV-65
e. Copper Oxides (I and II) Produced During an Elec- trolysis of 48% Hydrogen Fluoride.	LiClO <sub>4</sub> - Propylene Carbonate	IV-66
f. Copper Sulfide Thin Film.	N-Phenyl-N,N,N-tri- methylammonium Hexa- fluorophosphate-Di- methylformamide	IV-67
g. Antimony Trifluoride Pressed Cathodes.	LiClO <sub>4</sub> - Propylene Carbonate	IV-68, IV-69
h. Cupric Fluoride Pressed Cathodes Containing Antimony Trifluoride and Carbon Additives.	LiClO <sub>4</sub> - Propylene Carbonate	IV-70
i. Silver Oxide - Antimony Trifluoride Pressed Cathode.	LiClO <sub>4</sub> - Propylene Carbonate	IV-71

FIGURE 4a. LINEARLY VARYING POTENTIAL SCANS OF CUPRIC FLUORIDE SINTERED IN A NITROGEN ATMOSPHERE ON A VARIETY OF SUBSTRATES.  $\text{LiClO}_4$ -PROPYLENE CARBONATE ELECTROLYTES (1 MOLAL). LI COUNTER ELECTRODES. Ag/AgCl REFERENCE ELECTRODES. AREA OF SUBSTRATES =  $2.8\text{cm}^2$ \*.  $50\text{mv/sec}$  SCAN RATE.



\* The substrates were not completely covered with  $\text{CuF}_2$ .

FIGURE 4b. LINEARLY VARYING POTENTIAL SCANS OF CUPRIC FLUORIDE SINTERED ON ALUMINUM IN A NITROGEN ATMOSPHERE.  $\text{LiClO}_4$ -PROPYLENE CARBONATE ELECTROLYTE (1 MOLAL).  $\text{Li}$  COUNTER ELECTRODE.  $\text{Ag}/\text{AgCl}$  REFERENCE ELECTRODE. AREA OF SUBSTRATE =  $2.8\text{cm}^2$ .  $50\text{mv}/\text{sec}$  SCAN RATE.



\* The substrate was almost completely covered with  $\text{CuF}_2$ .

FIGURE 4c. LINEARLY VARYING POTENTIAL SCANS OF CUPRIC FLUORIDE SINTERED IN A METALLURGICAL PRESS ON SILVER EXPANDED METAL.  $\text{LiPF}_6$ -N-NITROSODIMETHYLAMINE ELECTROLYTE (1 MOLAL).  $\text{Li}$  COUNTER ELECTRODE.  $\text{Ag}/\text{AgCl}$  REFERENCE ELECTRODE. AREA OF SUBSTRATE =  $2.8\text{cm}^2$ .  $50\text{mv/sec}$  SCAN RATE.

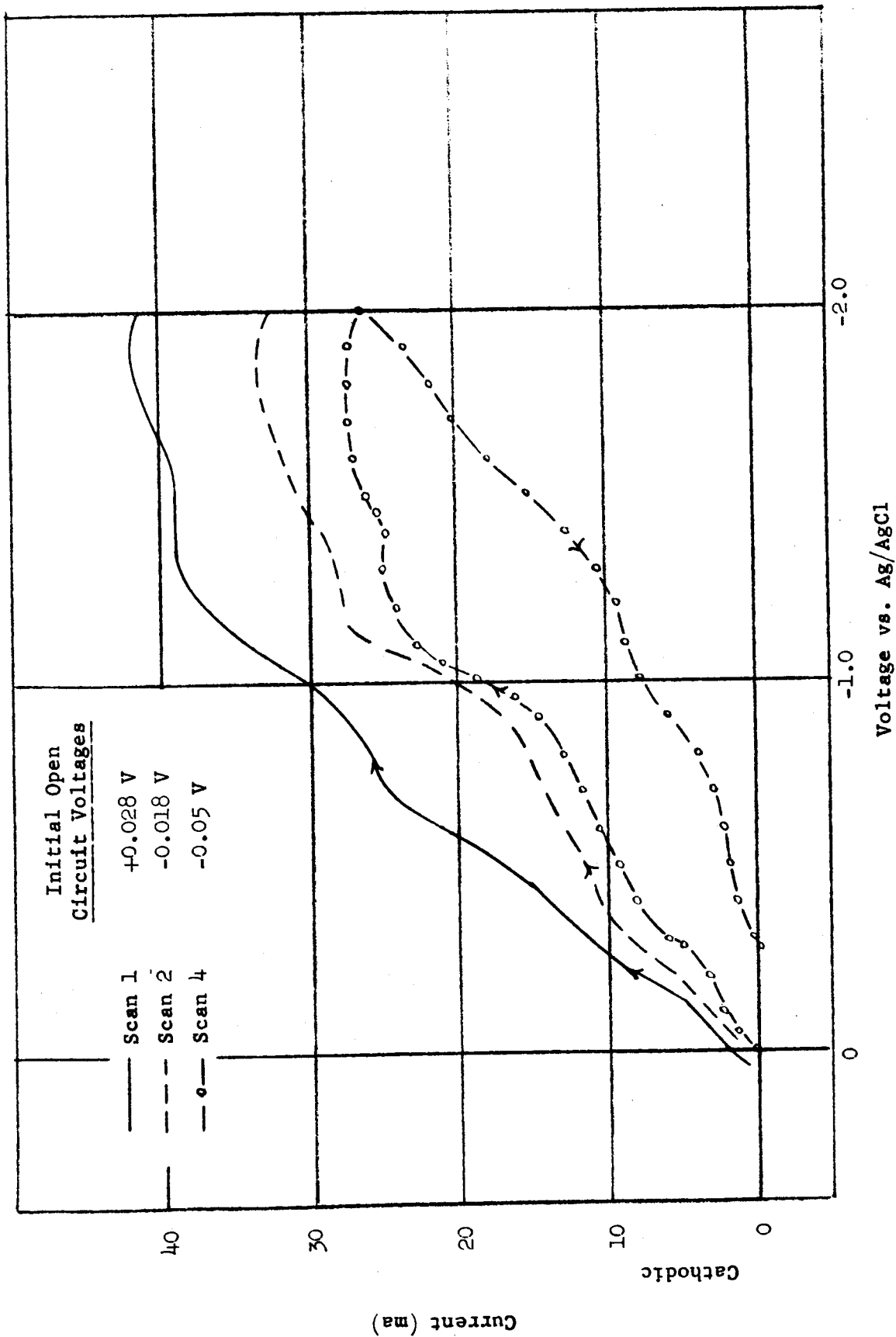
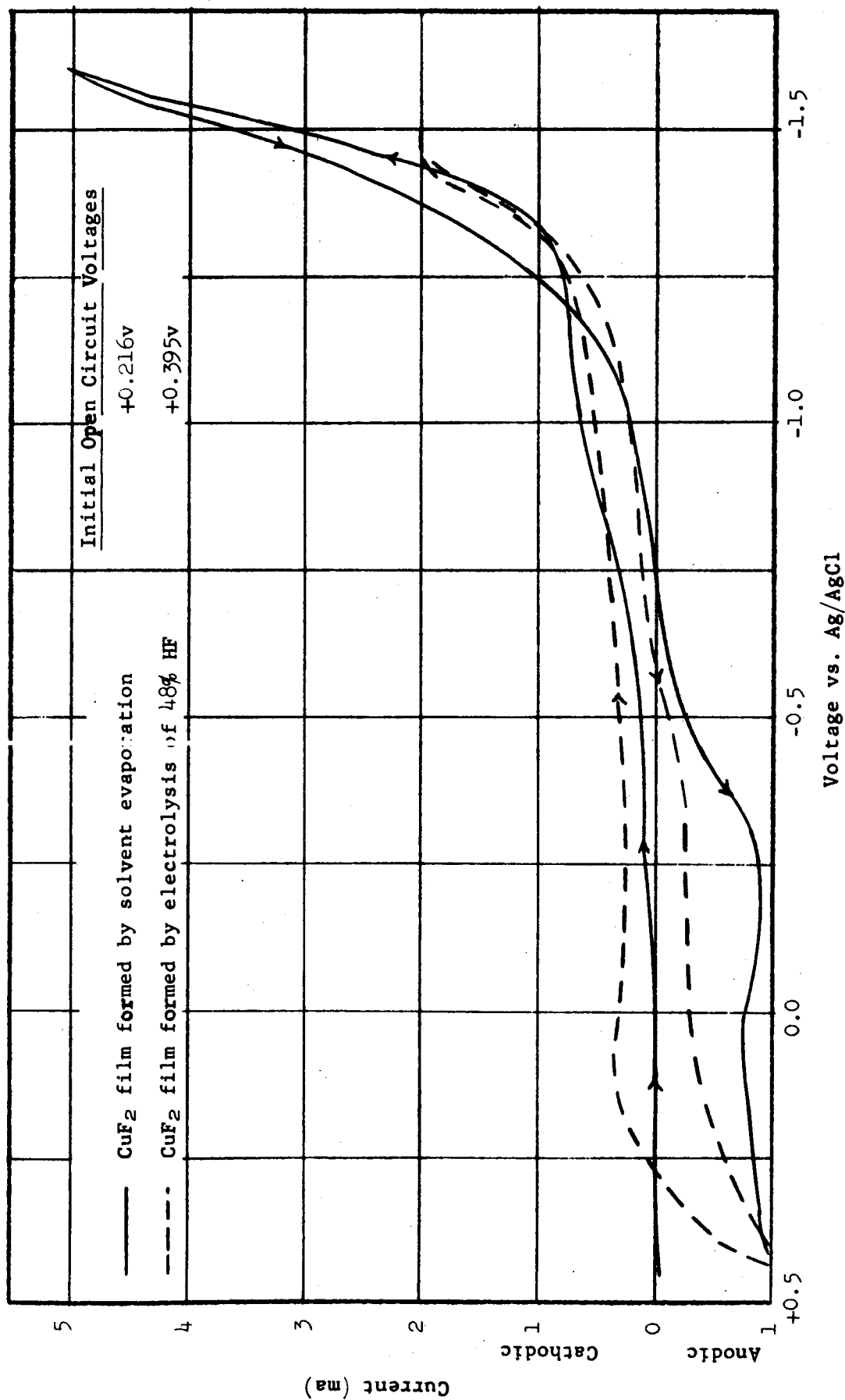


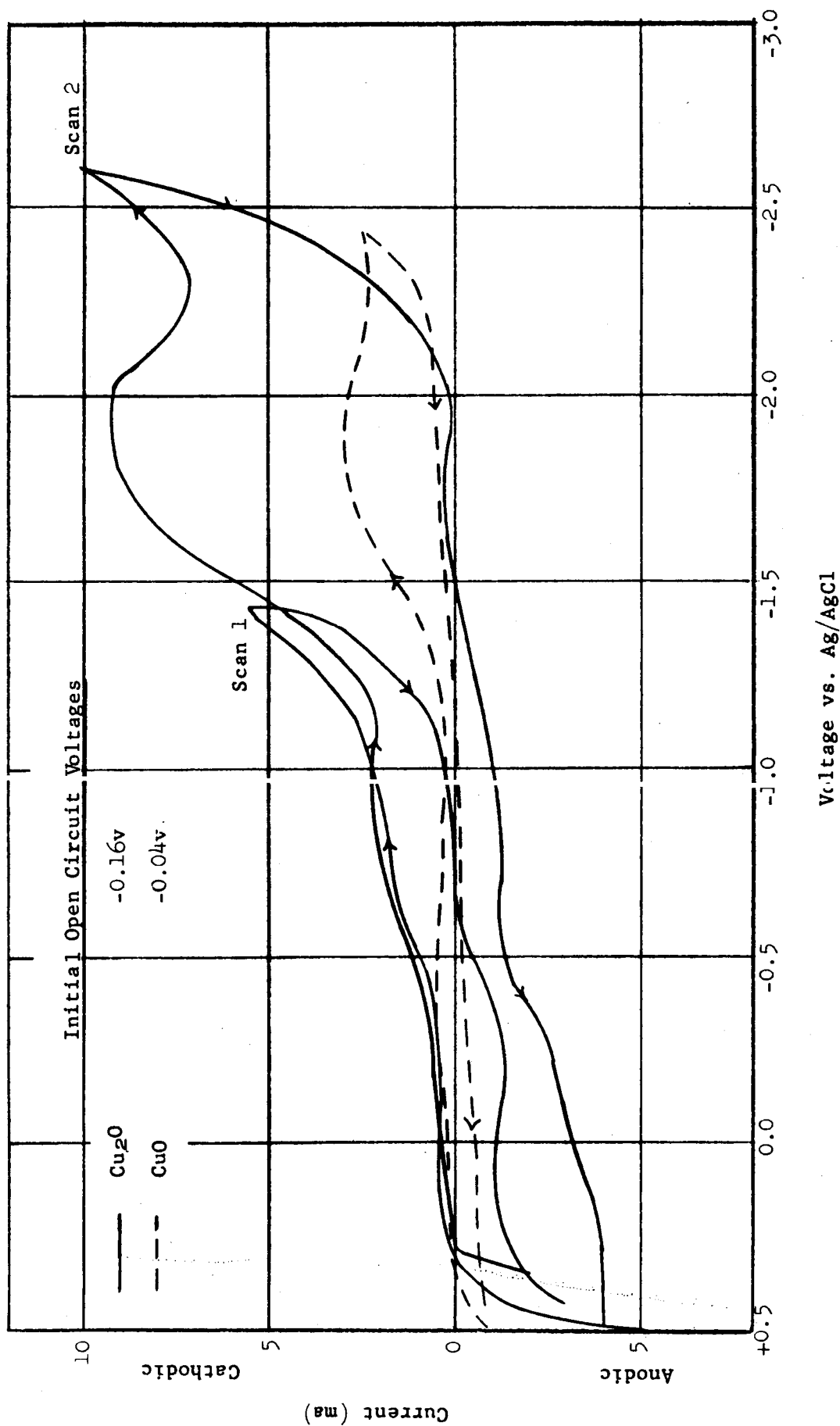
FIGURE 4d. LINEARLY VARYING POTENTIAL SCANS OF CUPRIC FLUORIDE THIN FILMS FORMED ON COPPER FOIL BY SOLVENT EVAPORATION AND BY ELECTROLYSIS OF 48% HF.\*  $\text{LiClO}_4$ -PROPYLENE CARBONATE ELECTROLYTES (1 MOLAL). Li COUNTER ELECTRODES. Ag/AgCl REFERENCE ELECTRODES. 50mv/sec SCAN RATE.



\* The area of the  $\text{CuF}_2$  electrodes was ca.  $0.5 \text{ cm}^2$ .



FIGURE 4e. LINEARLY VARYING POTENTIAL SCANS OF COPPER OXIDES (I AND II) PRODUCED DURING AN ELECTROLYSIS OF 48% HF. \*  $\text{LiClO}_4$ -PROPYLENE CARBONATE ELECTROLYTES (1 MOLAL). LI COUNTER ELECTRODES. Ag/AgCl REFERENCE ELECTRODES. 50 mv/sec SCAN RATE.



\* The area of the  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  electrodes was approximately 0.5  $\text{cm}^2$ .

FIGURE 4f. LINEARLY VARYING POTENTIAL SCANS OF A COPPER SULFIDE THIN FILM ELECTRODE IN A 1 MOLAL N-PHENYL-N,N,N-TRIMETHYLAMMONIUM HEXAFLUOROPHOSPHATE-DIMETHYLFORMAMIDE ELECTROLYTE. Li COUNTER ELECTRODE. AgS REFERENCE ELECTRODE. 50 mv/sec SCAN RATE.

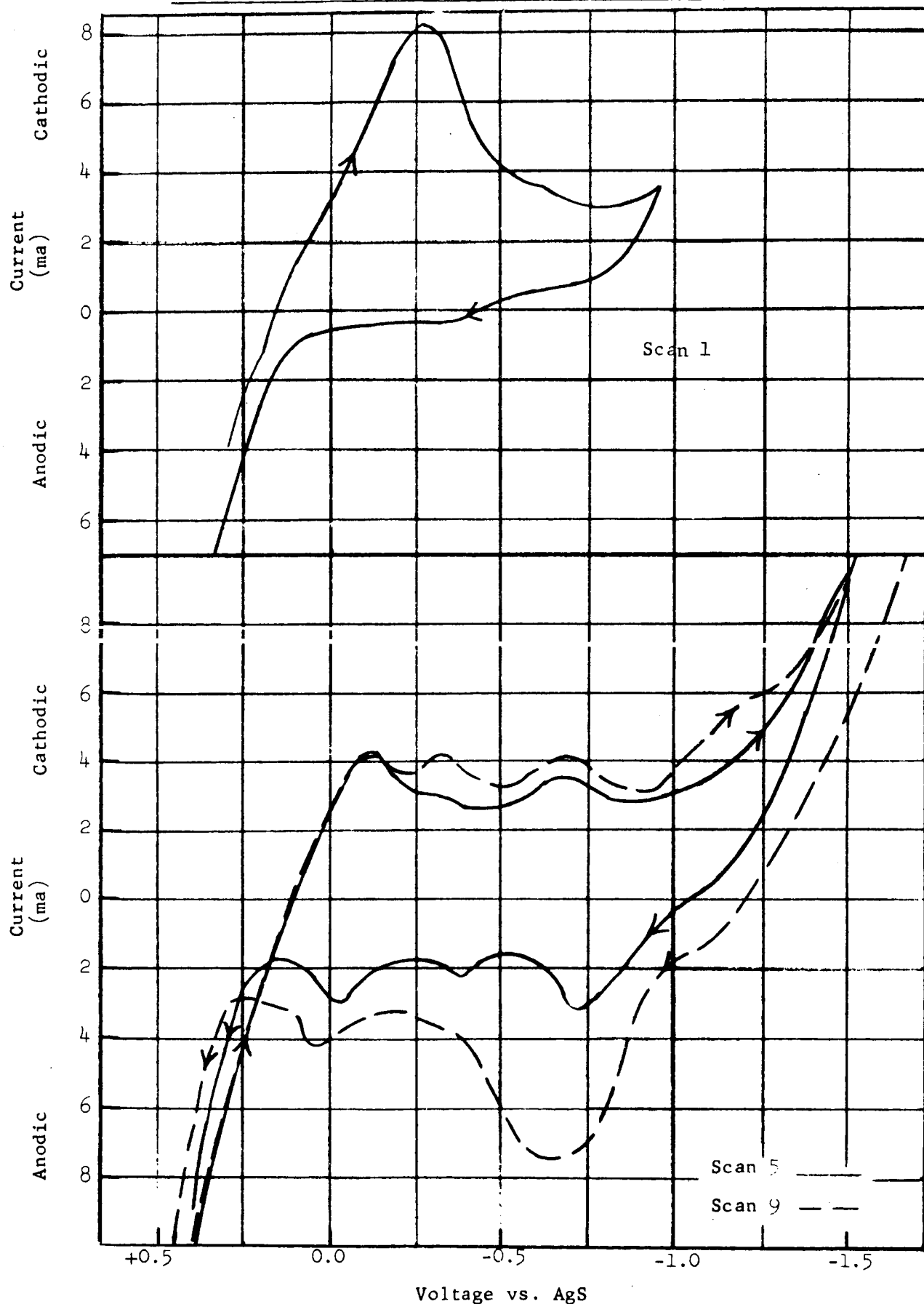


FIGURE 4g. LINEARLY VARYING POTENTIAL SCANS OF ANTIMONY TRIFLUORIDE PRESSED CATHODES.  $\text{LiClO}_4$ -PROPYLENE CARBONATE ELECTROLYTES (1 MOLAL).  $\text{Li}$  COUNTER ELECTRODES.  $\text{Ag}/\text{AgCl}$  REFERENCE ELECTRODES. SUBSTRATES -  $\text{Ag}$  EXPANDED METAL (AREA =  $1 \text{ cm}^2$ ). 50 mv/sec SCAN RATE.

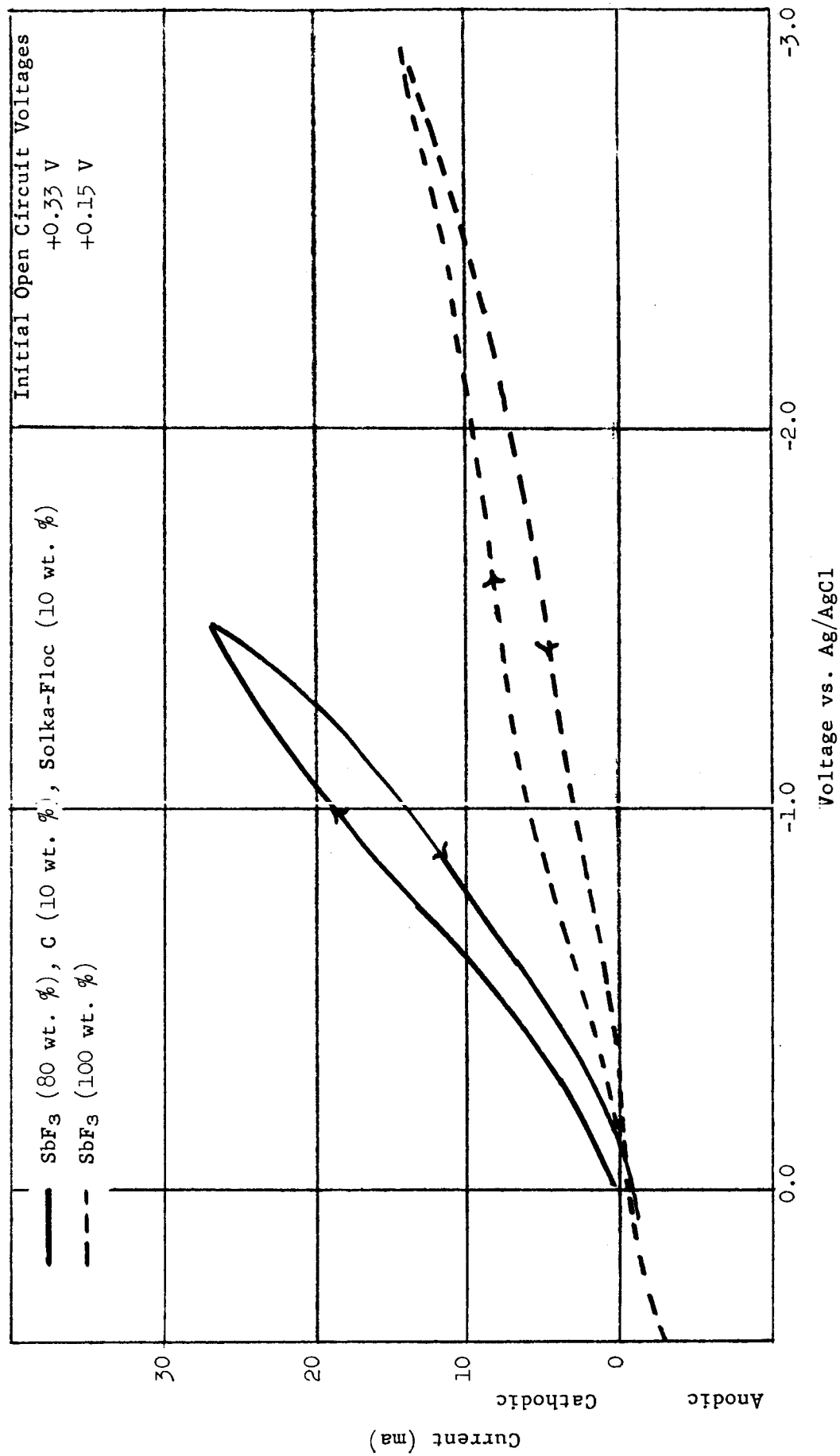


FIGURE 4g. (CONTINUED)

LINEARLY VARYING POTENTIAL SCANS OF ANTIMONY TRIFLUORIDE PRESSED CATHODES (80 WT. %  $\text{SbF}_3$ , 10 WT. % C, 10 WT. % SOLKA-FLOC).  $\text{LiClO}_4$ -PROPYLENE CARBONATE ELECTROLYTES (1 MOLAL). LI COUNTER ELECTRODES. Ag/AgCl REFERENCE ELECTRODES. SUBSTRATES - Ag AND Ni EXPANDED METAL (AREA =  $1 \text{ cm}^2$ ). 50 mv/sec SCAN RATE.

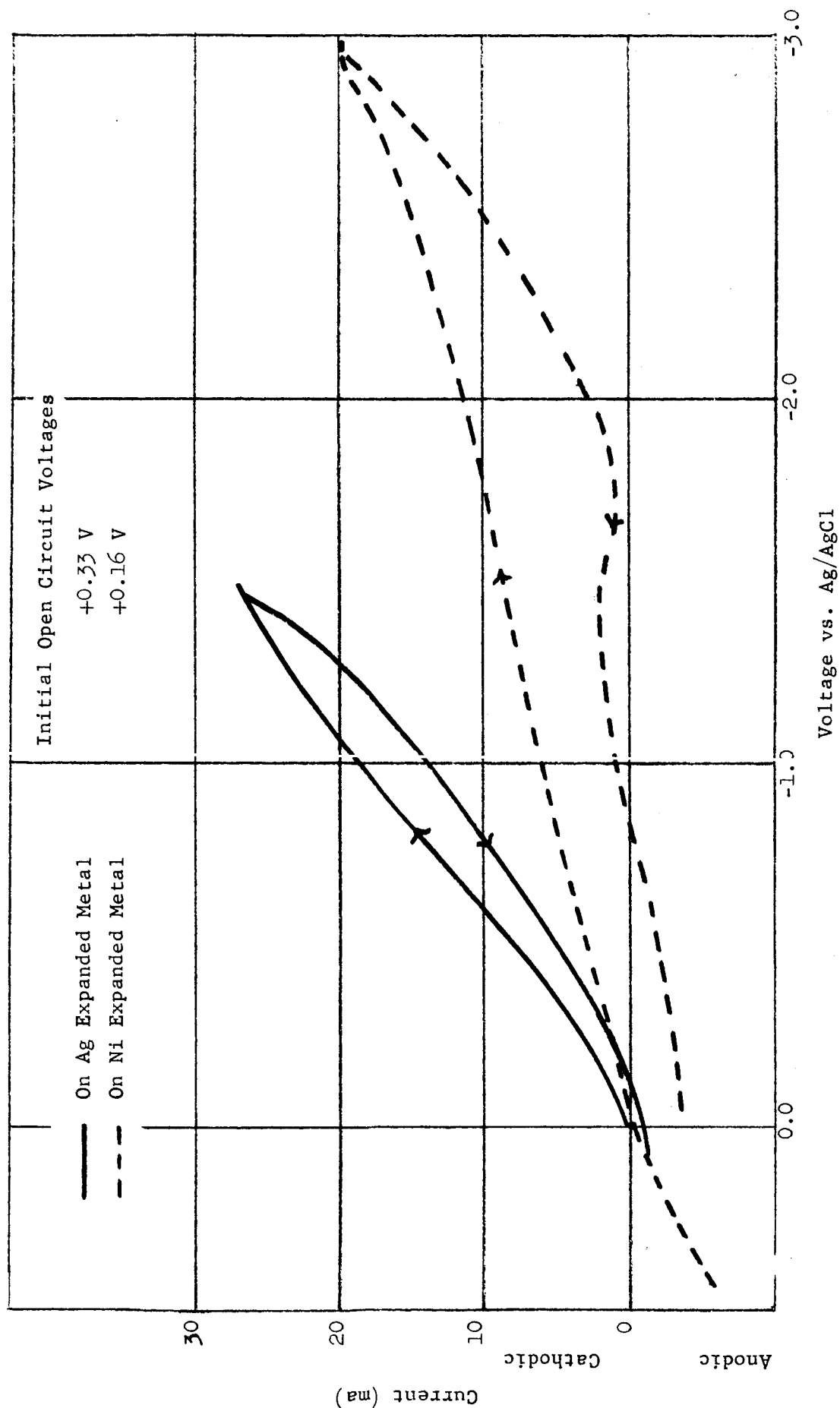


FIGURE 4h. LINEARLY VARYING POTENTIAL SCANS OF CUPRIC FLUORIDE PRESSED CATHODES CONTAINING ANTIMONY TRIFLUORIDE AND CARBON ADDITIVES.  $\text{LiClO}_4$ -PROPYLENE CARBONATE ELECTROLYTES (1 MOLAL). Li COUNTER ELECTRODES. Ag/AgCl REFERENCE ELECTRODES. SUBSTRATES - Cu EXPANDED METAL (AREA =  $1 \text{ cm}^2$ ). 50 mv/sec SCAN RATE.

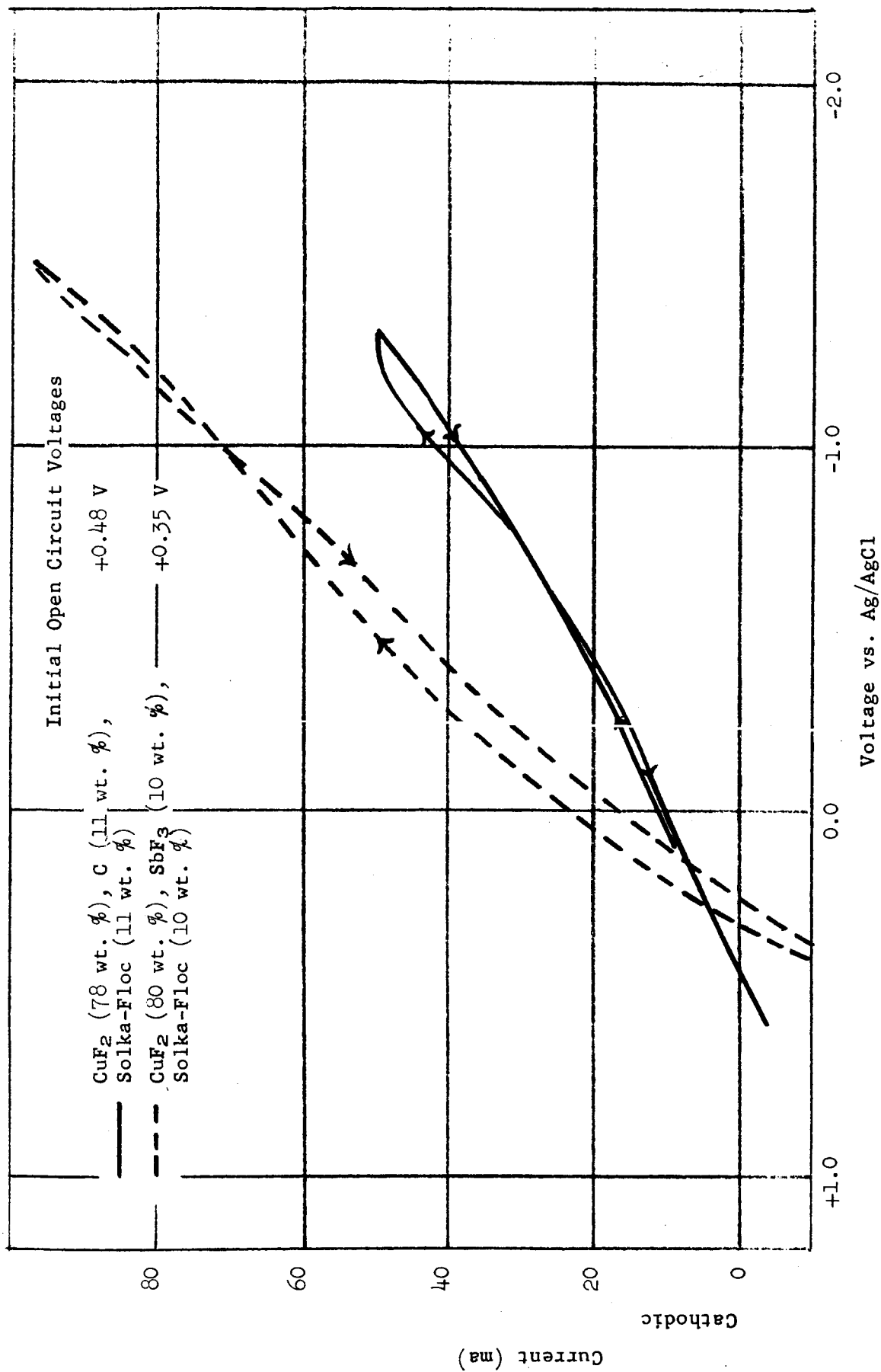


FIGURE 41. LINEARLY VARYING POTENTIAL SCAN OF A SILVER OXIDE-ANTIMONY TRIFLUORIDE PRESSED CATHODE (85.5 WT. % AgO, 10 WT. % SbF<sub>3</sub>, 4.5 WT. % SOLKA-FLOC). LiClO<sub>4</sub>-PROPYLENE CARBONATE ELECTROLYTE (1 MOLAL). LI COUNTER ELECTRODE. Ag/AgCl REFERENCE ELECTRODE. SUBSTRATE - Ag EXPANDED METAL (AREA = 1 cm<sup>2</sup>). 50 mv/sec SCAN RATE.

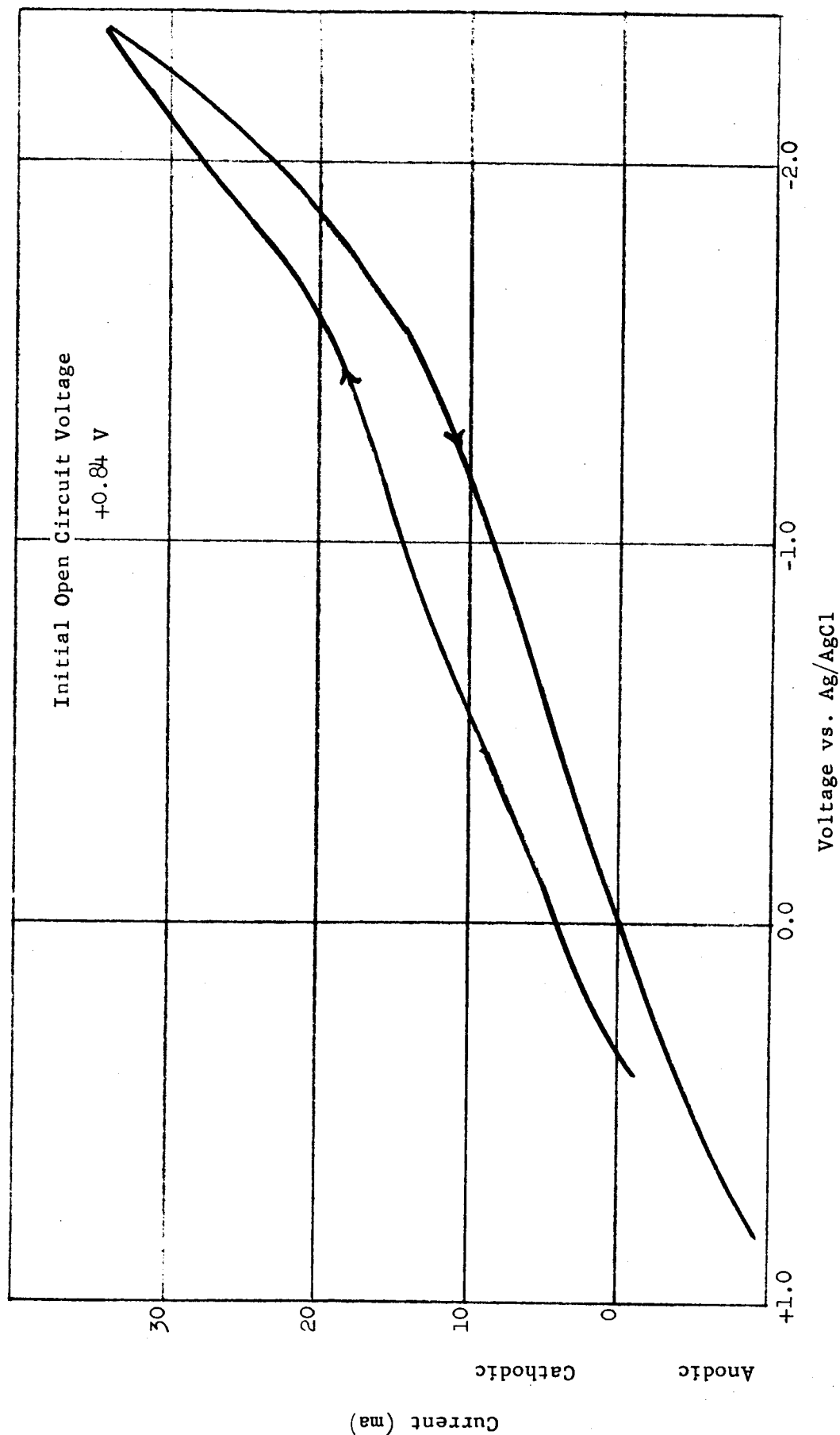


FIGURE 5. LINEARLY VARYING POTENTIAL STUDIES OF  
DISSOLVED ACTIVE ORGANIC CATHODE MATERIALS

<u>Cathode</u>	<u>Electrolyte (1 molal)</u>	<u>Page</u>
a. N-Chlorosuccinimide (0.1 and 1.0 molal)	LiPF <sub>6</sub> - Dimethylformamide	IV-73
b. 2,4 - Dinitrophenol (0.1 and 1.0 molal)	LiPF <sub>6</sub> - Dimethylformamide	IV-74
c. Trichloroisocyanuric Acid (0.1 molal)	AlCl <sub>3</sub> - Acetonitrile, LiPF <sub>6</sub> - Dimethylformamide	IV-75
d. Trichloromelamine (1 molal)	LiClO <sub>4</sub> - Propylene Carbonate	IV-76
e. Trichloromelamine Gel (1 molal)	LiPF <sub>6</sub> - Dimethylformamide	IV-77
f. Trichloromelamine (1 molal)	LiClO <sub>4</sub> - Propylene Carbonate, LiPF <sub>6</sub> - Dimethylformamide	IV-78
g. Trichloromelamine (0.1 and 1.0 molal)	LiPF <sub>6</sub> - Dimethylformamide	IV-79
h. Hexachloromelamine (0.1 molal)	LiPF <sub>6</sub> - Dimethylformamide	IV-80

FIGURE 5a. LINEARLY VARYING POTENTIAL SCANS OF TWO CONCENTRATIONS OF N-CHLOROSUCCINIMIDE IN A 1 MOLAL LIPF<sub>6</sub>-DIMETHYLFORMAMIDE ELECTROLYTE. SPEER CARBON WORKING AND COUNTER ELECTRODES (Area = 1 cm<sup>2</sup>). Ag/AgCl REFERENCE ELECTRODES. 50 mv/sec SCAN RATE.

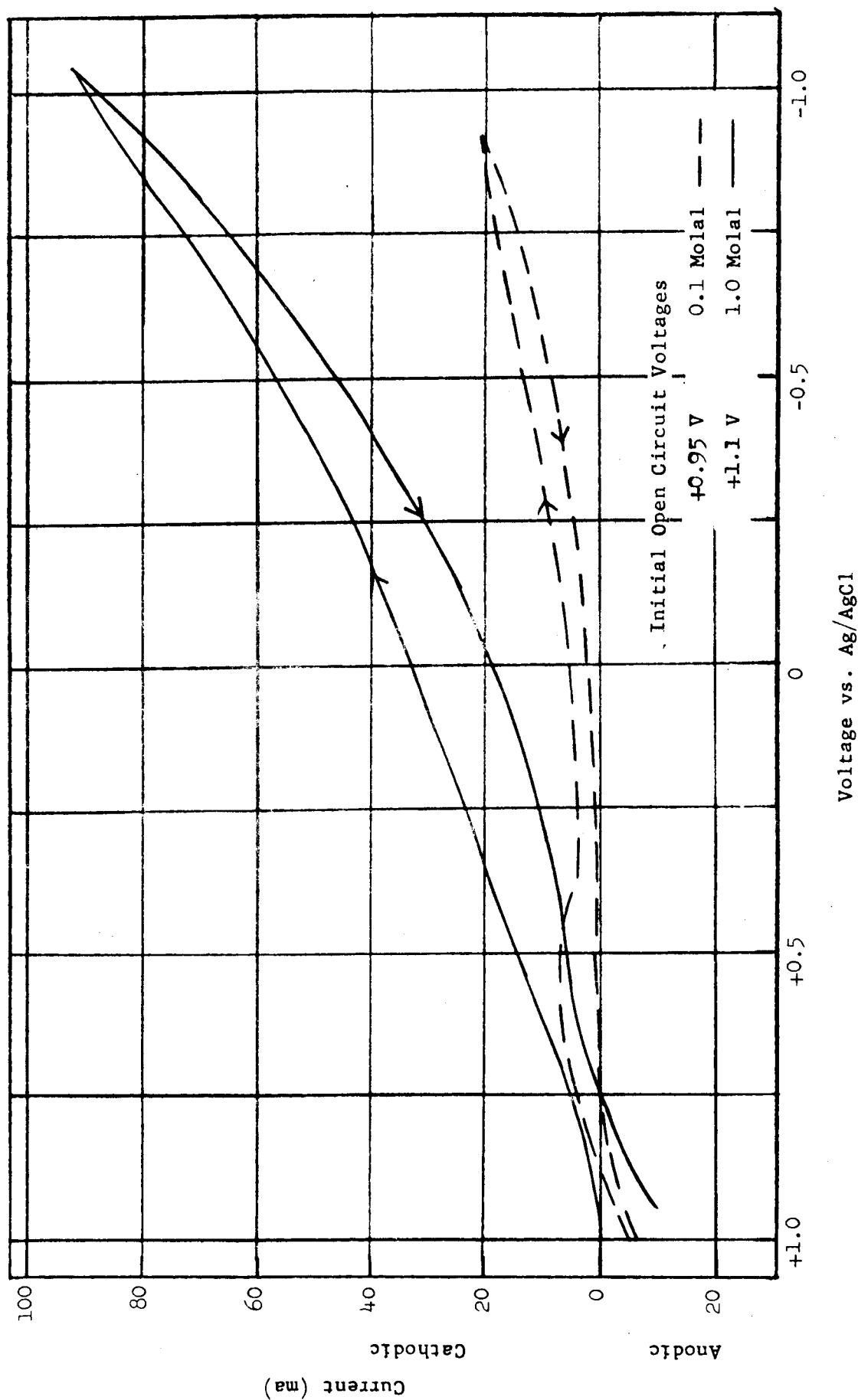




FIGURE 5b. LINEARLY VARYING POTENTIAL SCANS OF TWO CONCENTRATIONS OF 2,4-DINITROPHENOL IN A 1 MOLAL  $\text{LiPF}_6$ -DIMETHYLFORMAMIDE ELECTROLYTE. SPEER CARBON WORKING AND COUNTER ELECTRODES (Area =  $1 \text{ cm}^2$ ). Ag/AgCl REFERENCE ELECTRODES. 50 mv/sec SCAN RATE.

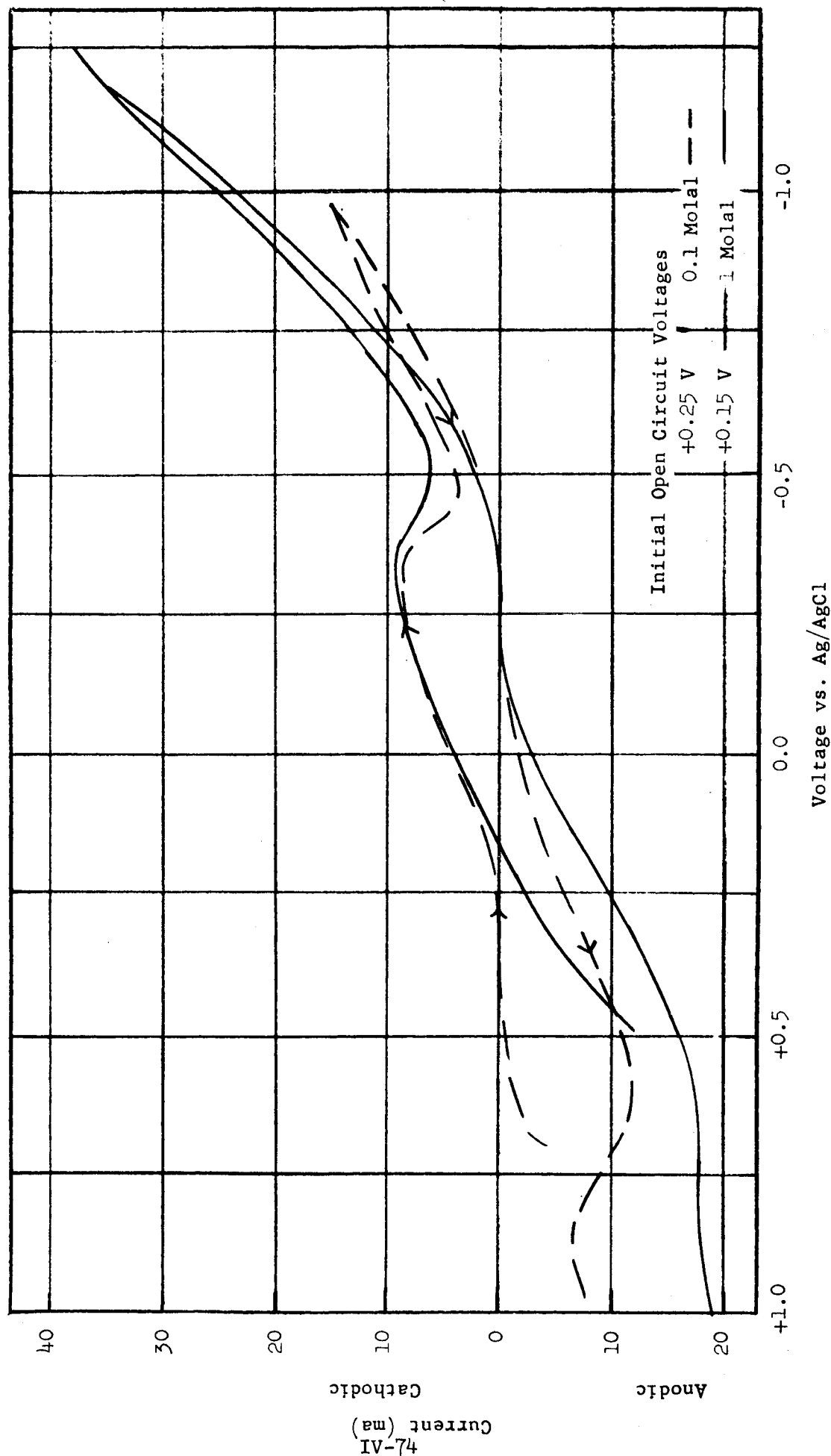


FIGURE 5c. COMPARISON OF LINEARLY VARYING POTENTIAL SCANS OF 0.1 MOLAL TRICHLOROISOCYANURIC ACID (ACL-85) IN 1 MOLAL  $\text{AlCl}_3$ -ACETONITRILE AND  $\text{LiPF}_6$ -DIMETHYLFORMAMIDE ELECTROLYTES. SPEER CARBON WORKING AND COUNTER ELECTRODES. (AREA  $1 \text{ cm}^2$ ).  $\text{Ag}/\text{AgCl}$  REFERENCE ELECTRODES. 50 mv/sec SCAN RATE.

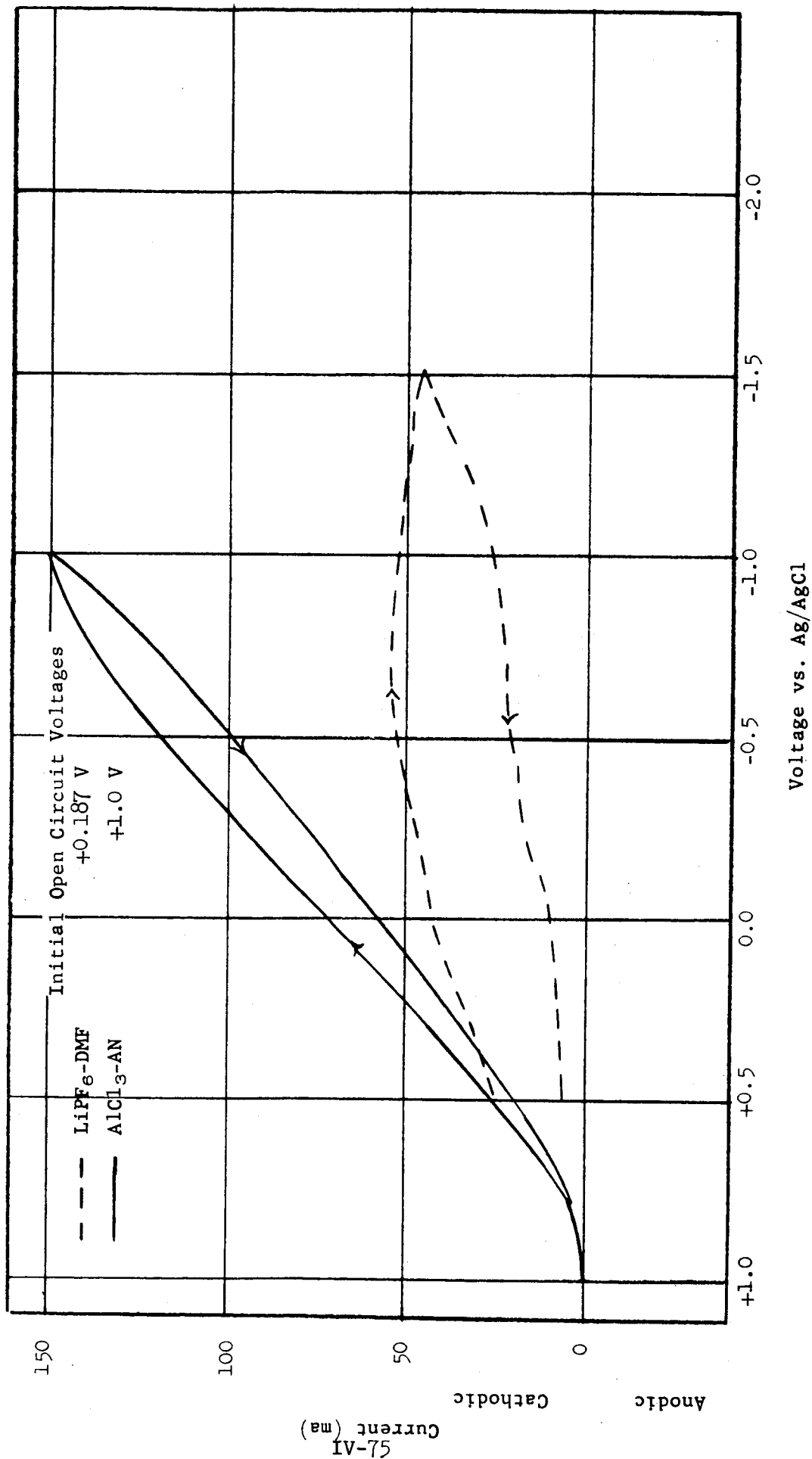


FIGURE 5d. LINEARLY VARYING POTENTIAL SCANS OF 1 MOLAL TRICHLOROMELAMINE IN A 1 MOLAL  $\text{LiClO}_4$ -PROPYLENE CARBONATE ELECTROLYTE. SPEER CARBON WORKING AND COUNTER ELECTRODES (AREA =  $1 \text{ cm}^2$ ).  $\text{Ag}/\text{AgCl}$  REFERENCE ELECTRODE. 50 mv/sec SCAN RATE.

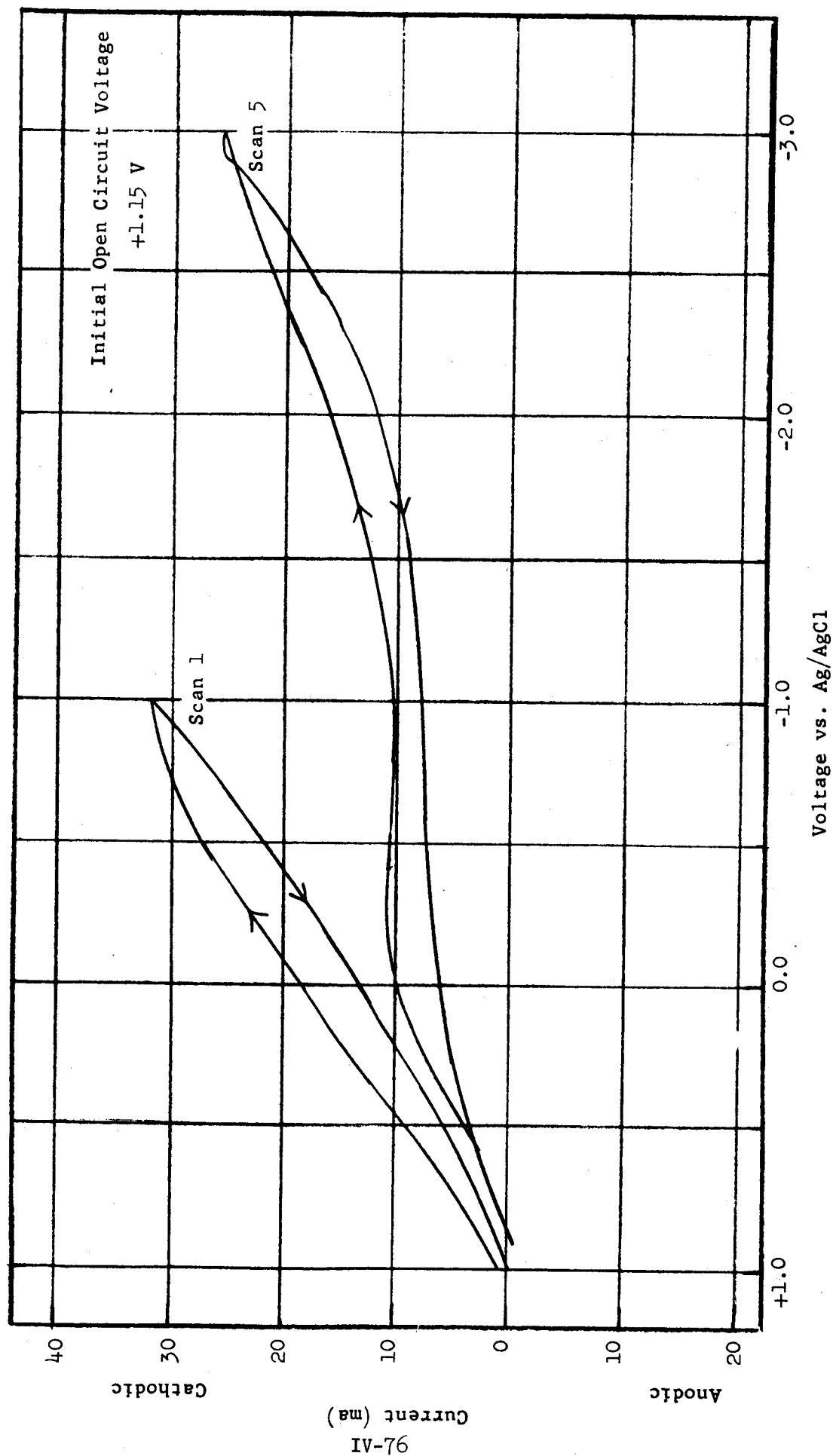


FIGURE 5e. LINEARLY VARYING POTENTIAL SCANS OF 1 MOLAL TRICHLOROMELAMINE IN A 1 MOLAL  $\text{LiPF}_6$ -DIMETHYLFORMAMIDE ELECTROLYTE.  $\text{Li}$  COUNTER ELECTRODE.  $\text{Ag}$  WORKING AND REFERENCE ELECTRODES (AREA =  $1 \text{ cm}^2$ ). 50 mv/sec SCAN RATE.

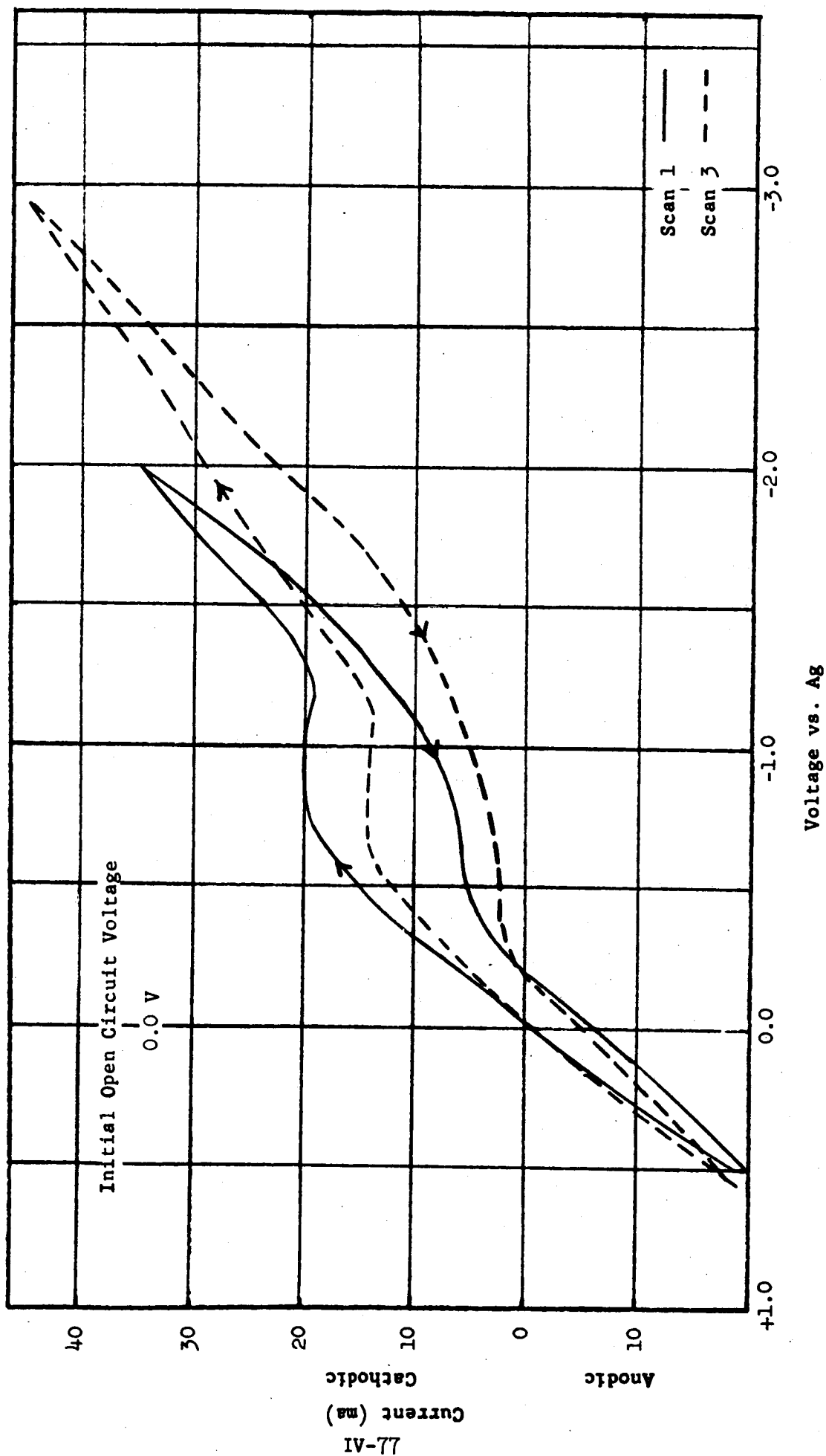


FIGURE 5f. COMPARISON OF LINEARLY VARYING POTENTIAL SCANS OF 1 MOLAL TRICHLOROMELAMINE IN 1 MOLAL  $\text{LiClO}_4$ -PROPYLENE CARBONATE AND  $\text{LiPF}_6$ -DIMETHYLFORMAMIDE ELECTROLYTES. SPEER CARBON WORKING AND COUNTER ELECTRODES (AREA =  $1\text{ cm}^2$ ) AND  $\text{Ag}/\text{AgCl}$  REFERENCE ELECTRODE IN  $\text{LiClO}_4$ -PC.  $\text{Ag}$  WORKING AND REFERENCE ELECTRODES (AREA =  $1\text{ cm}^2$ ) AND  $\text{Li}$  COUNTER ELECTRODE IN  $\text{LiPF}_6$ -DMF. 50 mv/sec SCAN RATE.

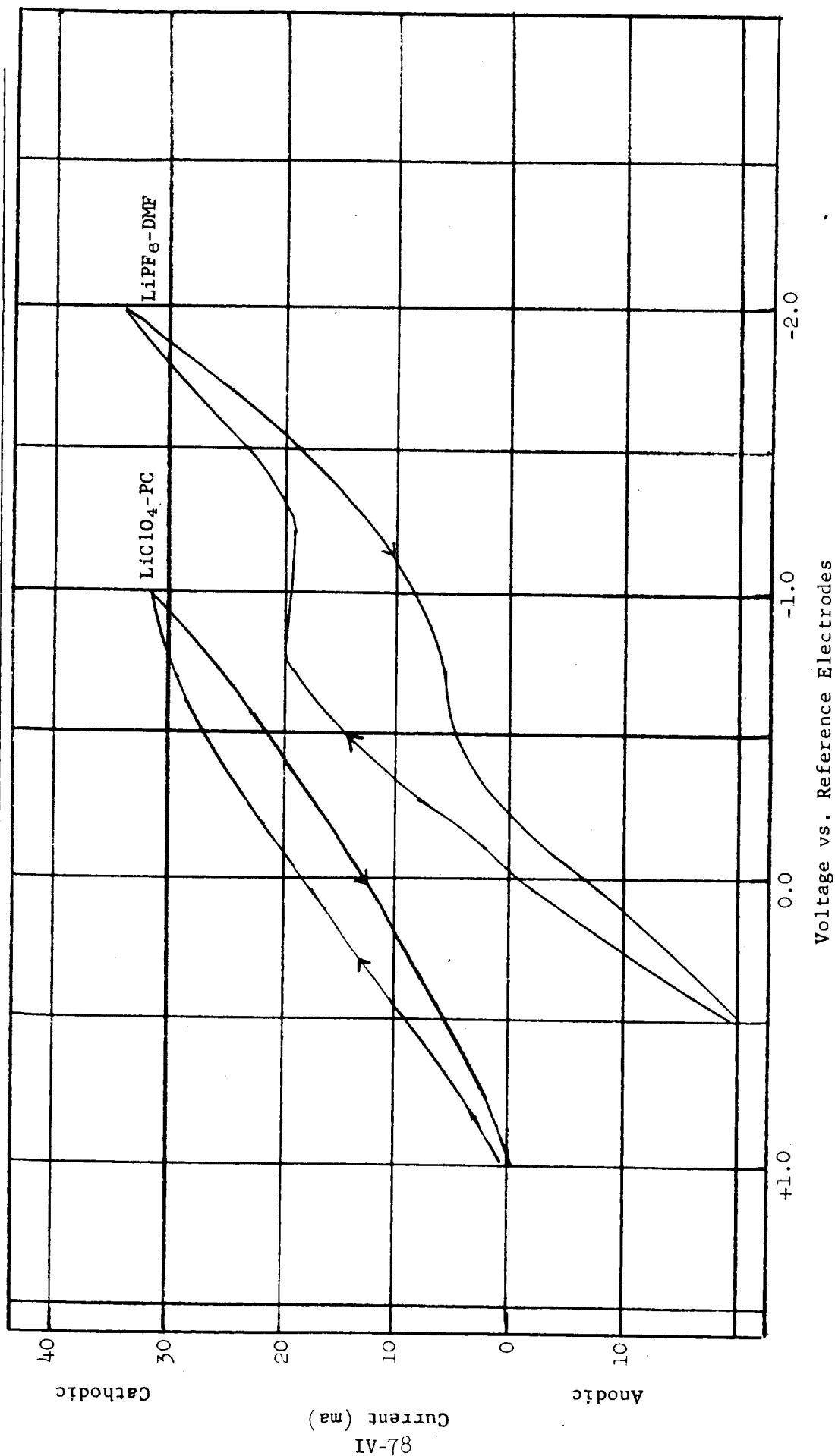


FIGURE 5g.

LINEARLY VARYING POTENTIAL SCANS OF TWO CONCENTRATIONS OF TRICHLOROMELAMINE (TCM) IN A 1 MOLAL  $\text{LiPF}_6$ -DIMETHYLFORMAMIDE ELECTROLYTE. SPEER CARBON WORKING AND COUNTER ELECTRODES (AREA =  $1 \text{ cm}^2$ ) FOR 0.1 MOLAL TCM. Ag WORKING AND Li COUNTER ELECTRODES FOR 1.0 MOLAL TCM (AREA =  $1 \text{ cm}^2$ ). Ag/AgCl REFERENCE ELECTRODE FOR 0.1 MOLAL TCM. Ag REFERENCE ELECTRODE FOR 1.0 MOLAL TCM. 50 mv/sec SCAN RATE.

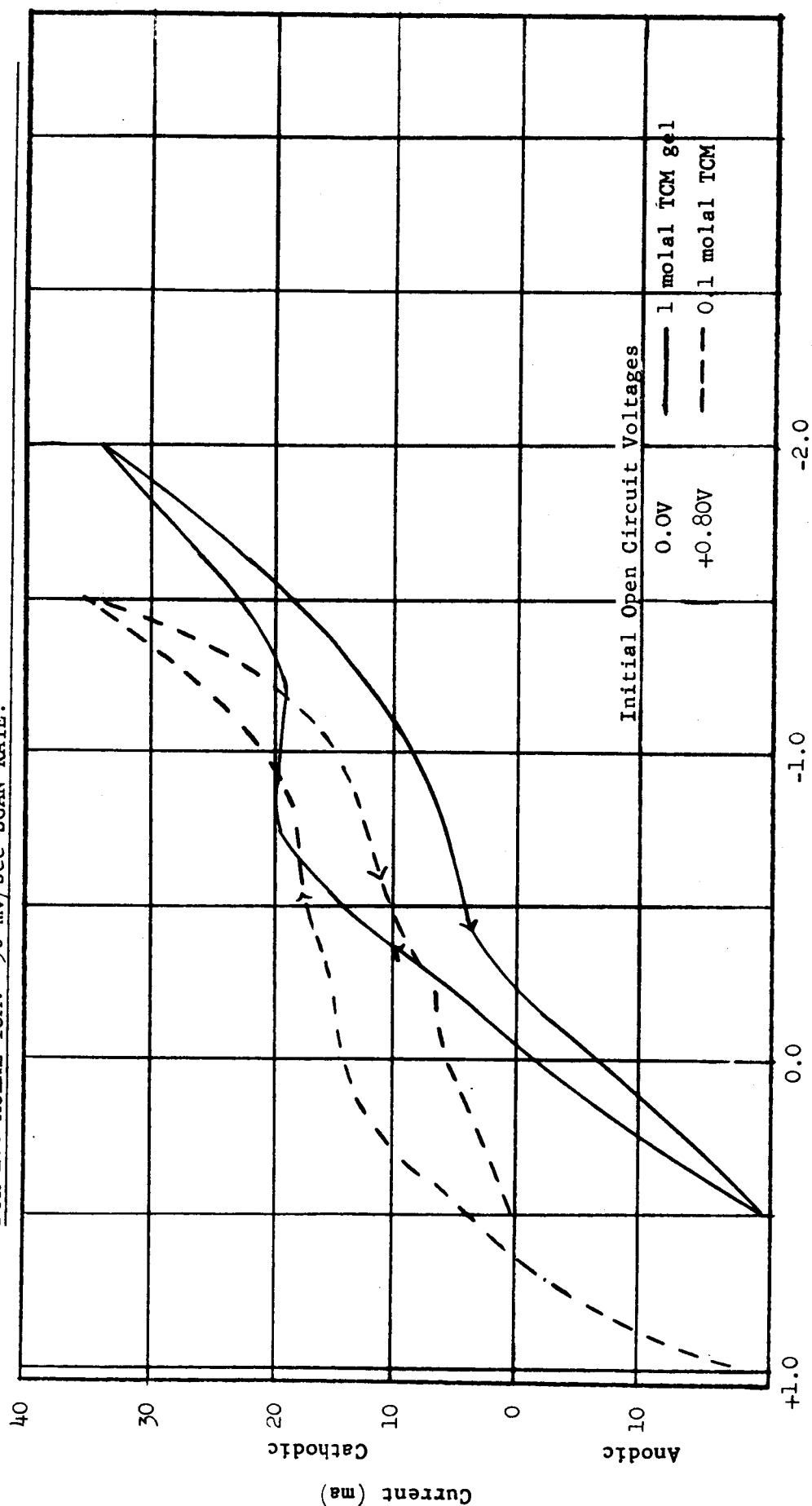


FIGURE 5h. LINEARLY VARYING POTENTIAL SCANS OF 0.1 MOLAL HEXACHLOROMELAMINE IN A 1 MOLAL LiPF<sub>6</sub>-DIMETHYLFORMAMIDE ELECTROLYTE. SPEER CARBON WORKING AND COUNTER ELECTRODES (AREA = 1 cm<sup>2</sup>). Ag/AgCl REFERENCE ELECTRODE. 50 mv/sec SCAN RATE.

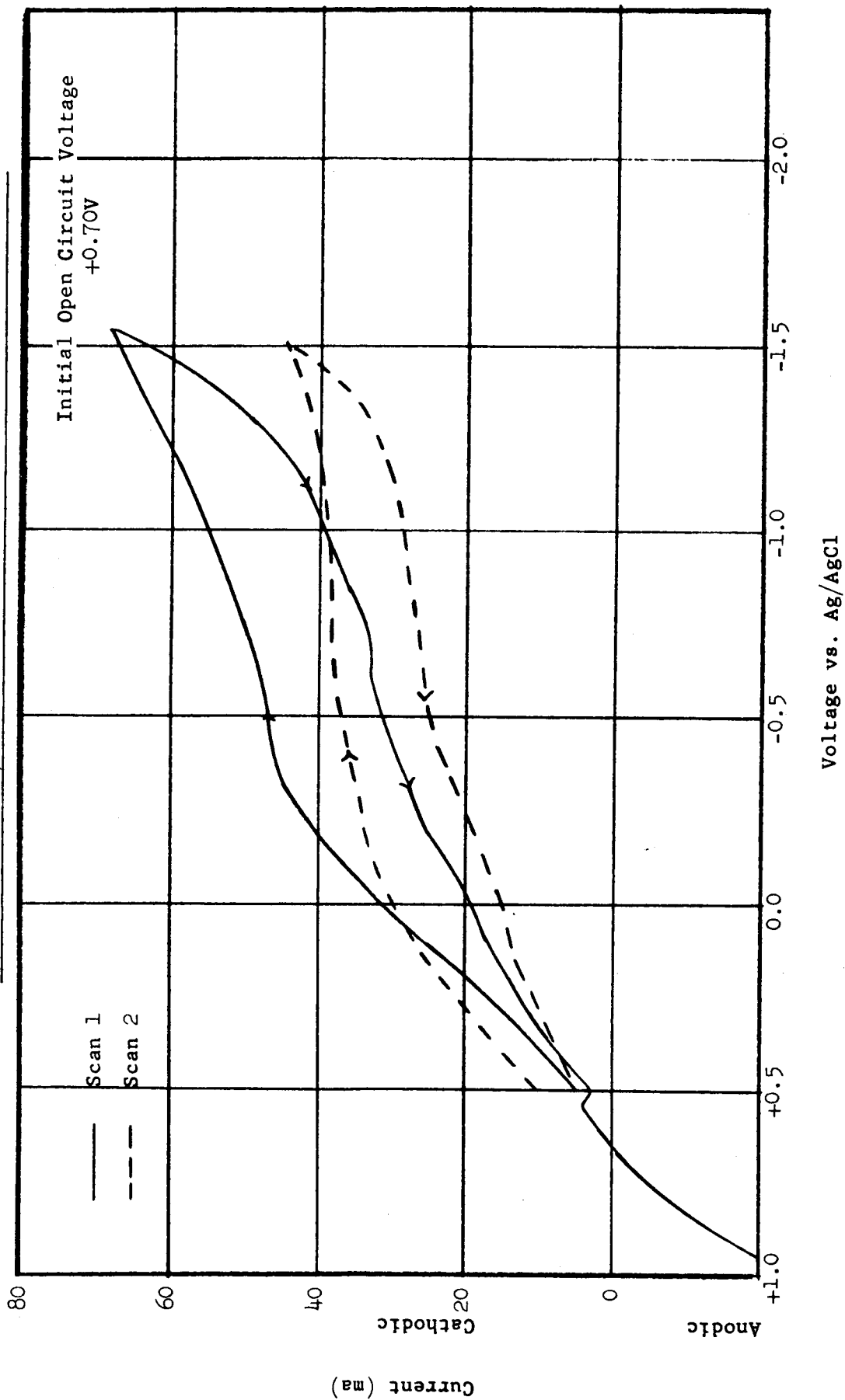


TABLE VII. DISTILLATION AND TESTING OF SOLVENTS  
EMPLOYED IN ELECTROLYTIC SOLUTIONS

N-Nitrosodimethylamine\*

A. Refractive Indices of Distilled Solvent Fractions at 25°C.

<u>Fraction</u>	<u>Original</u>	<u>One Week</u>	<u>Two Weeks</u>	<u>Four Weeks</u>	<u>Twelve Weeks</u>
Undistilled Sample	1.4339	1.4339	1.4340	1.4340	1.4341
1. (Discard)	---	---	---	---	---
2. (100 ml)	**	1.4344	1.4344	1.4345	1.4344
3. (100 ml)	**	1.4344	1.4344	1.4346	1.4346
4. (100 ml)	**	1.4343	1.4345	1.4345	1.4345
5. (100 ml)	**	1.4344	1.4344	1.4345	1.4345
6. (100 ml)	**	1.4345	1.4344	1.4346	1.4345

B. Specific Conductivities of Distilled Solvent Fractions (24-28°C).

Undistilled Sample	$2.64 \times 10^{-5}$	$9.95 \times 10^{-6}$	$1.34 \times 10^{-5}$	$1.78 \times 10^{-5}$	$6.78 \times 10^{-5}$
1. (Discard)	---	---	---	---	---
2. (100 ml)	**	$1.25 \times 10^{-5}$	$7.59 \times 10^{-5}$	$7.90 \times 10^{-5}$	$1.26 \times 10^{-4}$
3. (100 ml)	**	$2.18 \times 10^{-6}$	$9.3 \times 10^{-6}$	$6.88 \times 10^{-5}$	$8.90 \times 10^{-5}$
4. (100 ml)	**	$3.41 \times 10^{-6}$	$1.05 \times 10^{-5}$	$5.28 \times 10^{-5}$	$7.57 \times 10^{-5}$
5. (100 ml)	**	$3.34 \times 10^{-6}$	$2.96 \times 10^{-5}$	$6.53 \times 10^{-5}$	$7.47 \times 10^{-5}$
6. (100 ml)	**	$1.05 \times 10^{-5}$	$5.15 \times 10^{-5}$	$8.16 \times 10^{-5}$	$1.46 \times 10^{-4}$

\*  $n_D^{18.4} = 1.43743$ , Handbook of Chem. & Physics, Chem. Rubber Co., 44th Ed.

\*\* Not measured.



FIGURE 6. LINEARLY VARYING POTENTIAL STUDIES OF ELECTROLYTE DECOMPOSITION

6a. COMPARISON OF LINEARLY VARYING POTENTIAL SCANS OF 1 MOLAL  $\text{LiClO}_4$ -PROPYLENE CARBONATE ELECTROLYTES.  $\text{Ag/AgCl}$  REFERENCE ELECTRODES. 50 mv/sec SCAN RATE.

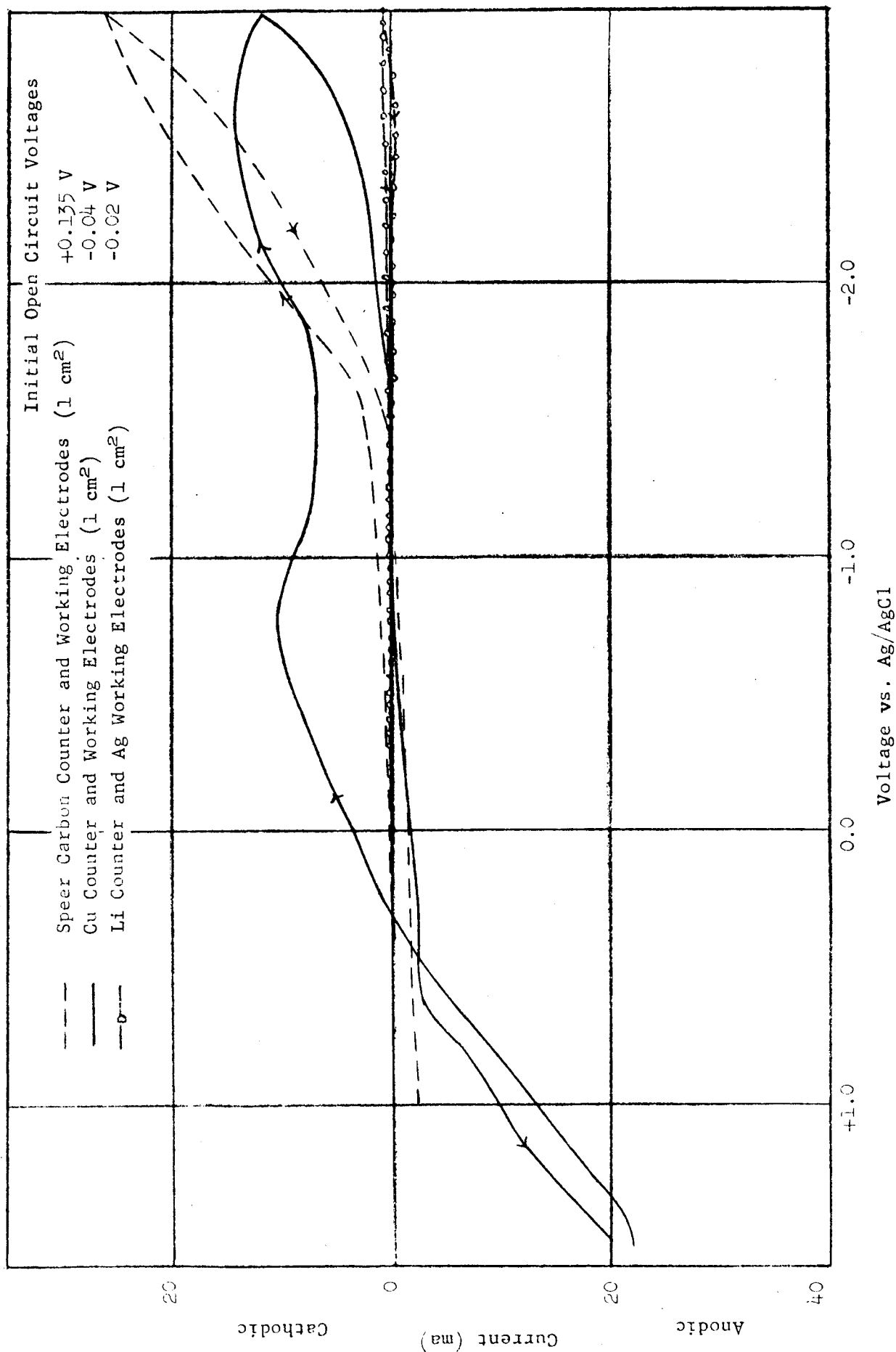


FIGURE 6. LINEARLY VARYING POTENTIAL STUDIES OF ELECTROLYTE DECOMPOSITION (Continued)

6b. COMPARISON OF LINEARLY VARYING POTENTIAL SCANS OF 1 MOLAL  $\text{LiCl-DIMETHYLFORMAMIDE}$  ELECTROLYTES.  $\text{Ag/AgCl}$  REFERENCE ELECTRODES. 50 mv/sec SCAN RATE.

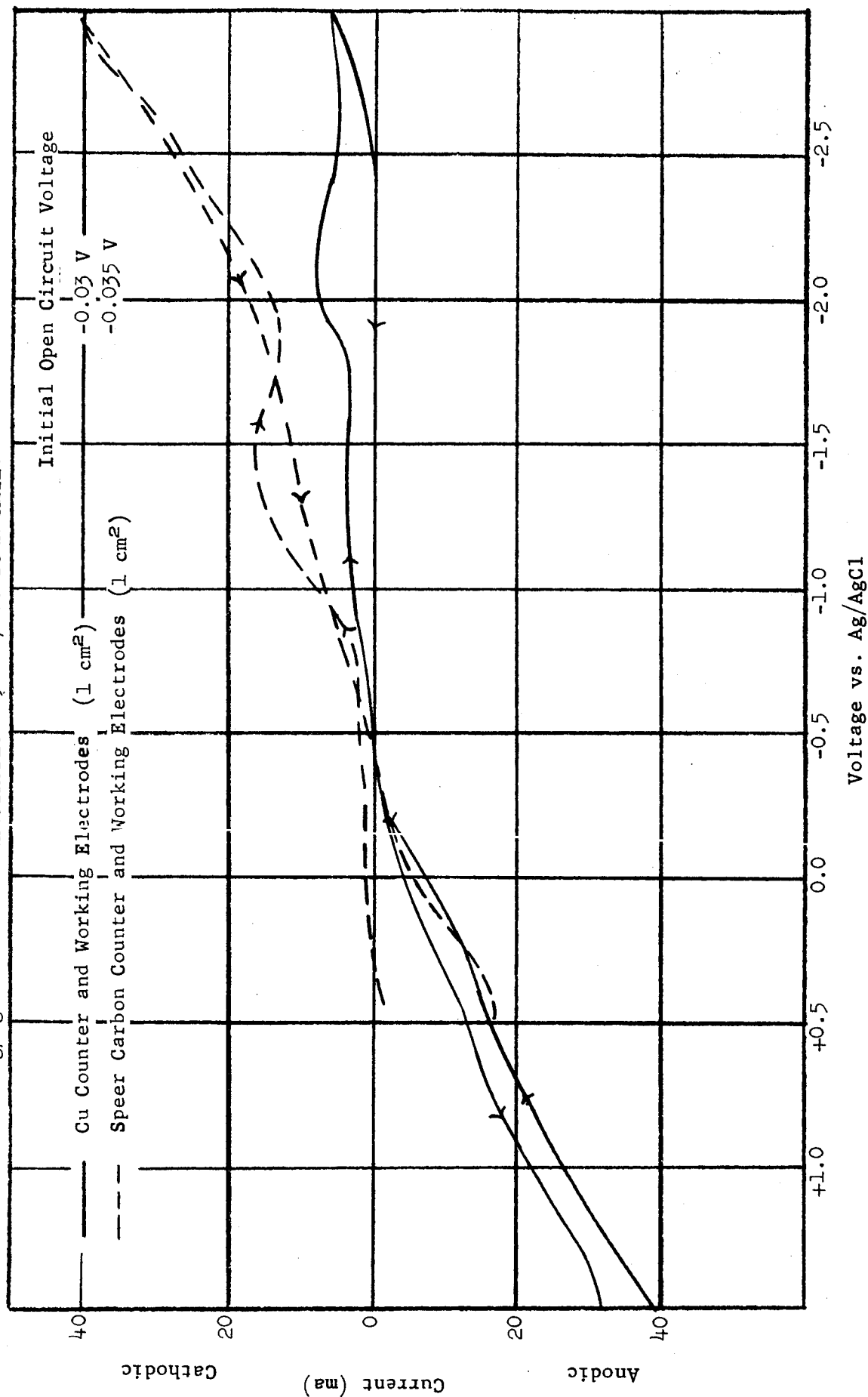


FIGURE 6. LINEARLY VARYING POTENTIAL STUDIES OF ELECTROLYTE DECOMPOSITION (Continued)

6c. A COMPARISON OF LINEARLY VARYING POTENTIAL SCANS OF 1 MOLAL N-PHENYL-N,N-TRIMETHYLAMMONIUM HEXAFLUOROPHOSPHATE-DIMETHYLFORMAMIDE ELECTROLYTES. Ag/AgCl REFERENCE ELECTRODES. 50 mv/sec SCAN RATE.

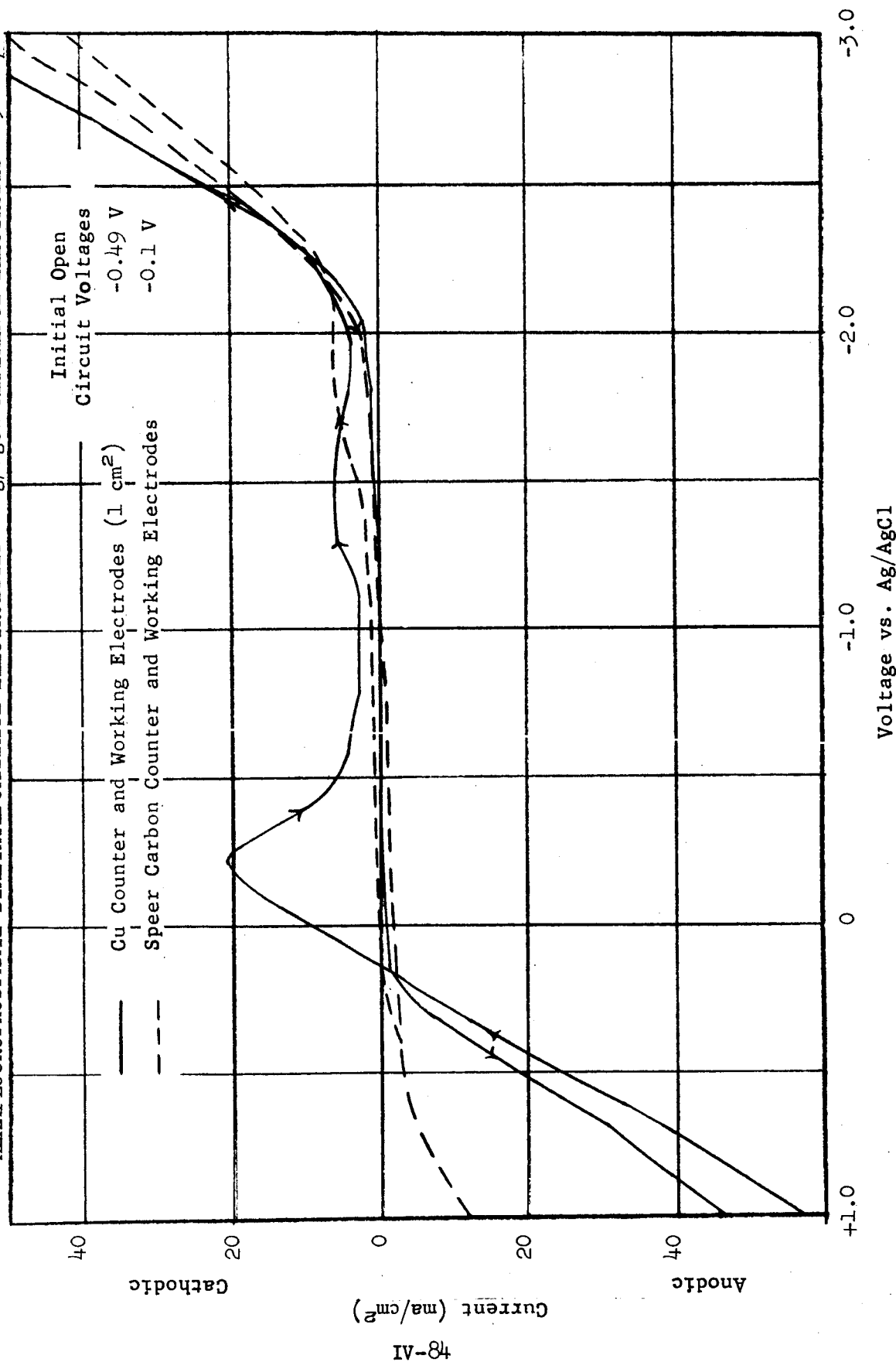


TABLE VIII. FULL CELL TESTING UTILIZING SEPARATOR MATERIALS

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B. Filter Paper Separator	IV-90
C. Epoxy Membrane Separator	IV-92

TABLE VIII. FULL CELL TESTING UTILIZING SEPARATOR MATERIALS

A. Anion Exchange Membrane Separators

1. Cell Details:

Anode - lithium. Area = ca. 0.5 cm<sup>2</sup>.

Cathode - CuCl<sub>2</sub>·2H<sub>2</sub>O (saturated) in 1 molal N-phenyl-N,N,N-trimethylammonium hexafluorophosphate  $[(C_6H_5)(CH_3)_3NPF_6]$ -dimethylformamide (DMF).

Cathodic current collector - Cu foil. Area = ca. 0.5 cm<sup>2</sup>.

Electrolyte - 1 molal (C<sub>6</sub>H<sub>5</sub>)(CH<sub>3</sub>)<sub>3</sub>NPF<sub>6</sub>-DMF

Membrane - E-7083 fuel cell membrane (Ionics, Inc.) equilibrated in DMF.

Reference electrodes - Ag/AgCl.

Cell construction - The membrane was placed between two polypropylene blocks. The blocks were bolted together so that a 1x1x1 cm well was located on each side of the membrane.

Time (Minutes)	Cell Voltage	Anode Voltage vs. Reference Electrode*	Cathode Voltage vs. Reference Electrode**	Anode Refer- ence Electrode vs. Cathode Ref- erence Electrode	Current (ma)
0	3.16	-3.05	+0.07	-0.17	0.0
6	3.17	-3.05	-0.06	-0.17	0.0
11	2.65	-2.93	-0.21	+0.13	1.2
15	2.63	-2.93	-0.21	+0.13	1.3
22	2.24	-2.79	-0.23	+0.31	2.0
27	2.15	-2.78	-0.25	+0.36	2.0
30	0.91	-2.64	-0.63	+1.12	5.0
36	0.86	-2.68	-0.63	+1.26	5.0
38	0.07	-2.62	-0.87	+1.83	7.1
43	0.13	-2.78	-0.98	+1.81	6.9
45	0.80	-2.79	-0.70	+1.30	5.0
50	0.81	-2.72	-0.65	+1.30	5.0
52	2.13	-2.84	-0.29	+0.40	2.0
57	2.13	-2.82	-0.29	+0.42	2.0
59	3.01	-2.97	-0.08	+0.03	0.0
69	2.94	-2.87	-0.07	-0.17	0.0
73	0.87	-2.67	-0.56	+1.26	5.0
82	0.86	---	---	+1.22	5.0

\* Located in the anolyte.

\*\* Located in the catholyte.

TABLE VIII. FULL CELL TESTING UTILIZING SEPARATOR  
MATERIALS (Continued)

A. Anion Exchange Membrane Separators (Continued)

1. (Continued)

Time (Minutes)	Cell Voltage	Anode Voltage vs. Reference Electrode*	Cathode Voltage vs. Reference Electrode**	Anode Refer- ence Electrode vs. Cathode Ref- erence Electrode	Current (ma)
88	0.85	---	---	+1.18	5.1
93	0.98	-2.65	-0.69	+1.03	4.8
113	1.08	-2.72	-0.62	+0.96	5.0
131	1.15	-2.65	-0.71	+0.78	5.0
146	1.23	-2.60	-0.70	+0.68	5.0
157	1.30	-2.56	-0.69	+0.57	5.0
169	1.32	-2.55	-0.68	+0.54	5.0
174	1.34	-2.51	-0.67	+0.53	5.0
185	1.27	-2.36	-0.65	+0.41	5.1

Observations: The original anolyte was clear and colorless. The catholyte, which was saturated with  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , was dark green. After the above test was completed, the cell was allowed to discharge for approximately 12 hours at a current of 5ma. At the end of this time, no leakage of the  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  solution into the anolyte was visually apparent. However, the lithium anode was covered with a black solid shown by X-ray diffraction to be Cu.

\* Located in the anolyte.

\*\* Located in the catholyte.

TABLE VIII. FULL CELL TESTING UTILIZING SEPARATOR  
MATERIALS (Continued)

A. Anion Exchange Membrane Separators(Continued)

2. Cell Details:

Anode - lithium. Area = ca. 0.5 cm<sup>2</sup>.

Cathode - CuCl<sub>2</sub>·2H<sub>2</sub>O (saturated) in 1 molal (C<sub>6</sub>H<sub>5</sub>)(CH<sub>3</sub>)<sub>3</sub>NPF<sub>6</sub>-N-nitrosodimethylamine (NDA).

Cathodic current collector - Cu foil. Area = ca. 0.5 cm<sup>2</sup>.

Electrolyte - 1 molal (C<sub>6</sub>H<sub>5</sub>)(CH<sub>3</sub>)<sub>3</sub>NPF<sub>6</sub>-NDA.

Membrane - E-7083 fuel cell membrane (Ionics, Inc.). The membrane, which was originally equilibrated in DMF, was equilibrated in NDA.

Reference electrodes - Ag/AgCl.

Cell construction - The membrane was placed between two polypropylene blocks. The blocks were bolted together so that a 1x1x1 cm well was located on each side of the membrane.

Time (Minutes)	Cell Voltage	Anode Voltage vs. Reference Electrode*	Cathode Voltage vs. Reference Electrode**	Anode Refer- ence Electrode vs. Cathode Ref- erence Electrode	Current (ma)
0	2.87	-2.73	-0.07	-0.22	0.0
5	2.87	-2.70	-0.06	-0.23	0.0
8	1.57	-2.58	-0.90	-0.10	2.0
13	1.53	-2.59	-1.15	-0.10	2.0
15	0.53	-2.50	-1.89	+0.10	5.0
20	0.49	-2.50	-1.91	+0.07	5.1
23	0.09	-2.46	-2.15	+0.24	8.0
28	0.06	-2.46	-2.16	+0.26	7.7
29	0.39	-2.51	-1.99	+0.12	5.0
34	0.36	-2.53	-2.03	+0.14	5.0
37	0.88	-2.61	-1.76	+0.03	2.0
42	0.86	-2.60	-1.63	+0.08	2.0
43	1.74	-2.72	-1.16	0.00	0.0
48	2.07	-2.70	-0.80	0.00	0.0
119	2.35	-2.74	-0.36	0.00	0.0

\* Located in the anolyte.

\*\* Located in the catholyte.

TABLE VIII. FULL CELL TESTING UTILIZING SEPARATOR MATERIALS (Continued)

A. Anion Exchange Membrane Separators (Continued)

2. (Continued)

<u>Time (Minutes)</u>	<u>Cell Voltage</u>	<u>Anode Voltage vs. Reference Electrode*</u>	<u>Cathode Voltage vs. Reference Electrode**</u>	<u>Anode Refer- ence Electrode vs. Cathode Ref- erence Electrode</u>	<u>Current (ma)</u>
167	2.32	-2.76	-0.37	0.00	0.0
169	0.28	-2.42	-1.73	+0.26	5.0
213	0.08	-2.48	-2.12	+0.28	4.2
281	0.05	-2.57	-2.08	+0.47	3.4
298	0.03	-2.58	-2.09	+0.48	3.2

Observations: The original anolyte was clear yellow. The catholyte, which was saturated with  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , was dark brown. During the 8 ma discharge a solid began to form between the Cu current collector and the reference electrode located in the catholyte. At the end of the test, a considerable amount of this solid was present in solution. The Cu foil was covered with black crystals which were identified by X-ray diffraction as Ag.

The lithium anode was covered with a gray film which was identified by X-ray diffraction as  $\text{LiOH}$ .

\* Located in the anolyte.

\*\* Located in the catholyte.



TABLE VIII. FULL CELL TESTING UTILIZING SEPARATOR  
MATERIALS (Continued)

B. Filter Paper Separator

1. Cell Details:

Anode - lithium

Cathode - silver oxide (95 wt. % Ag<sub>2</sub>O, 5 wt. % Solka-Floc);  
 area - 0.25 cm<sup>2</sup>.

Electrolyte - 1 molal (C<sub>6</sub>H<sub>5</sub>)(CH<sub>3</sub>)<sub>3</sub>NPF<sub>6</sub>-DMF.

Membrane - No. 40 Whatman filter paper.

Reference electrodes - Ag/AgCl.

Cell construction - the membrane was placed between two polypropylene blocks. The blocks were bolted together so that a 1x1x1 cm well was located on each side of the membrane.

<u>Time</u> <u>(Minutes)</u>	<u>Cell</u> <u>Voltage</u>	<u>Anode Voltage</u> <u>vs. Ag/AgCl</u> <u>Reference</u> <u>Electrode*</u>	<u>Cathode Voltage</u> <u>vs. Ag/AgCl</u> <u>Reference</u> <u>Electrode**</u>	<u>Anode Reference</u> <u>Electrode vs.</u> <u>Cathode Reference</u> <u>Electrode</u>	<u>Current</u> <u>(ma)</u>
0	3.7	-3.00	+0.54	0.00	0
0	2.4	---	---	+0.08	1.9
1	2.4	-2.80	-0.51	+0.08	1.9
6	2.3	-2.79	-0.57	+0.08	1.9
8	2.3	-2.80	-0.59	+0.08	1.9
10	1.8	-2.65	-0.81	+0.20	4.9
11	1.8	---	---	+0.20	4.9
12	1.8	-2.67	-0.81	+0.20	4.9
14	1.8	-2.68	-0.83	+0.20	4.9
15	1.1	-2.48	-1.12	+0.42	10.4
18	1.2	-2.54	-1.12	+0.42	10.4
21	1.2	-2.62	-1.12	+0.42	10.4
23	0.2	---	---	+0.80	20.0
24	0.2	-2.38	-1.50	+0.80	19.0
25	0.13	-2.42	-1.58	+0.84	18.0
27	0.13	---	---	+0.84	18.0
28	2.4	---	---	+0.04	0.0
29	2.6	-3.00	-0.57	+0.04	0.0
30	3.6	---	---	+0.04	0.0
36	1.1	---	---	+0.50	10.2
41	1.0	---	---	+0.53	10.2

\* Located in the anolyte.

\*\* Located in the catholyte.

TABLE VIII. FULL CELL TESTING UTILIZING SEPARATOR  
MATERIALS (Continued)

B. Filter Paper Separator (Continued)

<u>Time</u> <u>(Minutes)</u>	<u>Cell</u> <u>Voltage</u>	<u>Anode Voltage</u> <u>vs. Ag/AgCl</u> <u>Reference</u> <u>Electrode*</u>	<u>Cathode Voltage</u> <u>vs. Ag/AgCl</u> <u>Reference</u> <u>Electrode**</u>	<u>Anode Reference</u> <u>Electrode vs.</u> <u>Cathode Reference</u> <u>Electrode</u>	<u>Current</u> <u>(ma)</u>
46	1.0	---	---	+0.56	10.0
51	0.9	---	---	+0.60	10.0
56	0.8	---	---	+0.63	10.0
61	1.2	---	---	---	9.9
66	0.8	---	---	---	9.9
71	0.6	---	---	+2.0	9.8
76	0.6	---	---	+2.1	9.7
81	0.4	---	---	+2.2	9.7
86	0.4	---	---	+2.2	9.6
91	0.3	---	---	+2.3	9.9
96	0.2	---	---	+2.4	10.0
98	0.1	-2.67	0.00	+2.4	9.9
99	2.2	-3.08	0.00	+0.8	0.0

Observations: The catholyte darkened during the discharge. Leakage of the catholyte into the anolyte was not visually evident.

\* Located in the anolyte.

\*\* Located in the catholyte.

TABLE VIII. FULL CELL TESTING OF SEPARATOR  
MATERIALS (Continued)

C. Epoxy Membrane Separator

1. Cell Details:

Anode - lithium. Area = ca.  $0.5\text{cm}^2$ .

Cathode - ACL-85 (saturated) in 1 molal  $\text{LiPF}_6$ -DMF.

Cathodic current collector - Pyrolytic graphite rod. Area = ca.  $1\text{cm}^2$ ). After the first 2ma discharge it was replaced by HP-15 Speer carbon. (Area = ca.  $0.5\text{cm}^2$ ).

Electrolyte - 1 molal  $\text{LiPF}_6$ -DMF.

Membrane - Versapor epoxy No. 6429 (Gelman).

Reference electrodes - Ag screen

Cell construction - The membrane was placed between two polypropylene blocks. The blocks were bolted together so that a  $1\text{xlxlcm}$  well was located on each side of the membrane.

Time (Minutes)	Cell Voltage	Anode Voltage vs. Refer- ence Electrode*	Cathode Voltage vs. Refer- ence Electrode**	Anode Reference Electrode vs. Cathode Ref- erence Electrode	Current (ma)
0	4.25	-3.12	+1.09	0.00	0
15	4.17	-3.09	+1.02	-0.03	0
19	2.69	-3.02	-0.07	+0.27	2
25	2.50	-2.93	-0.23	+0.22	2
32	Cathodic current collector was replaced.				0
42	4.03	-3.00	+1.02	-0.05	0
45	2.59	-2.72	+0.16	+0.30	2
50	2.50	-2.69	+0.03	+0.25	2
55	0.80	-2.41	-1.09	+0.56	5
60	1.04	-2.43	-0.76	+0.67	5
65	0.99	-2.44	-0.83	+0.65	5
70	0.10	-2.25	-1.36	+0.81	7
75	0.11	-2.25	-1.39	+0.78	6
80	0.10	-2.23	-1.39	+0.76	6
81	2.33	-2.59	+0.02	+0.26	2
85	2.33	-2.62	0.00	+0.29	2
90	3.86	-2.94	+0.89	+0.03	0

\* Located in the anolyte

\*\* Located in the catholyte.

TABLE VIII. FULL CELL TESTING OF SEPARATOR MATERIALS (Continued)

C. Epoxy Membrane Separator (Continued)

<u>Time (Minutes)</u>	<u>Cell Voltage</u>	<u>Anode Voltage vs. Refer- ence Electrode*</u>	<u>Cathode Voltage vs. Refer- ence Electrode**</u>	<u>Anode Reference Electrode vs. Cathode Ref- erence Electrode</u>	<u>Current (ma)</u>
95	3.91	-2.97	+0.92	+0.05	0
100	3.96	-2.99	+0.93	+0.05	0
105	3.97	-2.98	+0.96	+0.05	0
110	3.97	-2.98	+0.97	+0.06	0
115	0.08	-2.11	-1.49	+0.55	6
125	0.07	-2.18	-1.65	+0.44	5
130	0.08	-2.13	-1.47	+0.59	6

Observations: The cell was allowed to discharge at a maximum current density level for 1-1/2 hours after the above test was completed. At this time the current had dropped to nearly 0 ma. The anolyte, which was originally clear, had become discolored. The bright yellow catholyte remained unchanged. A green-brown solid had formed on the Li anode. This substance was identified as LiAg by X-ray diffraction. Both reference electrodes were covered with a thin white film. The membrane remained intact and was yellow on the side facing the cathode.

---

\* Located in the anolyte.

\*\* Located in the catholyte.

TABLE IX. TWO WEEK STABILITY TESTS FOR CASE MATERIALS IN ELECTROLYTE SOLUTIONS

Case Material*	Solvent	Solute	Weight Before Test (g)	Weight After Two Weeks (g)	Observations
1. Polyethylene	Dimethylformamide (DMF)	None	0.1526	0.1533	No change.
2. Polyethylene	DMF	$\text{NH}_4\text{PF}_6$	0.1703	0.1712	No change.
3. Polyethylene	DMF	$\text{O} \begin{smallmatrix} \text{CH}_2\text{CH}_2 \\ \text{CH}_2\text{CH}_2 \end{smallmatrix} \text{NH}_2\text{PF}_6^{**}$	0.1551	0.1558	No change.
4. Polyethylene	DMF	$(\text{C}_6\text{H}_5)(\text{CH}_3)_3\text{NPF}_6^{***}$	0.1733	0.1742	No change.
5. Polyethylene	N-Nitrosodimethyl- amine (NDA)	None	0.1684	0.1690	No change.
6. Polyethylene	NDA	$\text{NH}_4\text{PF}_6$	0.1491	0.1498	No change.
7. Polyethylene	NDA	$\text{O} \begin{smallmatrix} \text{CH}_2\text{CH}_2 \\ \text{CH}_2\text{CH}_2 \end{smallmatrix} \text{NH}_2\text{PF}_6$	0.1614	0.1621	No change.
8. Polypropylene	DMF	None	0.1605	0.1614	No change.
9. Polypropylene	DMF	$\text{NH}_4\text{PF}_6$	0.1503	0.1508	No change.
10. Polypropylene	DMF	$\text{O} \begin{smallmatrix} \text{CH}_2\text{CH}_2 \\ \text{CH}_2\text{CH}_2 \end{smallmatrix} \text{NH}_2\text{PF}_6$	0.1595	0.1601	No change.
11. Polypropylene	DMF	$(\text{C}_6\text{H}_5)(\text{CH}_3)_3\text{NPF}_6$	0.1719	0.1723	No change.
12. Polypropylene	NDA	None	0.1234	0.1237	No change.
13. Polypropylene	NDA	$\text{NH}_4\text{PF}_6$	0.1309	0.1316	No change.
14. Polypropylene	NDA	$\text{O} \begin{smallmatrix} \text{CH}_2\text{CH}_2 \\ \text{CH}_2\text{CH}_2 \end{smallmatrix} \text{NH}_2\text{PF}_6$	0.1528	0.1531	No change.

\* Supplier - Cadillac Plastic.

\*\* Morpholinium hexafluorophosphate.

\*\*\* N-Phenyl-N,N-trimethylammonium hexafluorophosphate.

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